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Study Panel on Assessing Potential Ocean Pollutants
to the
Ocean Affairs Board
Commission on Natural Resources
National Research Council

NATIONAL ACADEMY OF SCIENCES
WASHINGTON, D.C. 1975

1a

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The members of the committee selected to undertake this project and prepare this report were chosen for recognized scholarly competence and with due consideration for the balance of disciplines appropriate to the project. Responsibility for the detailed aspects of this report rests with that committee.

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PREFACE

Environmental scientists are increasingly required to meet situations calling for expert application of scientific data to solve concrete, complex problems. Unfortunately, substantial, relevant information, when in existence, is often hard to find. In many instances it must be traced to obscure file drawers, industry or government publications of limited distribution, or enigmatic indexing in the open literature. Even when such information is collected and combined with data drawn from field observations, a synthesis resulting in a coherent solution is often elusive.

In the face of these obstacles, a group of environmental scientists(1) met in July 1972 to seek out procedures for predicting which materials might jeopardize future ocean resources. Potential radioactive marine pollutants had been successfully predicted in the past, and other sets of pollutants had been defined by such events as the Minimata Bay mercury poisoning and the pesticide deaths of non-target organisms. However, the thousands of substances that enter the ocean system through industrial, agricultural, or domestic activities have remained largely unexamined. Which of these, if any, might have an undesirable environmental impact?

The enormous field of possible contaminants was narrowed by considering four parameters: production rate, environmental persistence, toxicity, and bioaccumulation. The group chose four substances for a trial investigation: mercury, polychlorinated biphenyls, and asbestos--all defined as pollutants--and tetracycline, a representative of biologically-active pharmaceuticals. The test study procedure was as follows:

1. The chemical characteristics of the potential pollutant that would make it dangerous in the marine environment were determined.
2. Production of the material and its release to the environment were evaluated, and, if the material occurred in nature, the man-induced and natural fluxes in the environment were compared.
3. Transport of the material within the environment was assessed by examining data from the atmosphere, rivers, sewer outfalls, marine waters, and dredged materials.
4. Concentrations and residence times of the material in such environmental reservoirs as the atmosphere, mixed and deep ocean layers, and biosphere were estimated.
5. The ultimate environmental fate of the materials were studied.

At a meeting in September 1972,(2) the results of the above inquiry and the possibility of assembling a collection of relevant data on potential ocean pollutants were considered. New approaches to pollution problems were developed. At a meeting at the Massachusetts Institute of Technology in January 1973,(3) a consensus had been reached to nominate a study panel and to select an investigative procedure. It was hoped that these investigations, although they did not necessarily address critical current problems, would provide guidelines for a more comprehensive assessment in the future.

Experience with the first four chemicals indicated that the data gathering task would require considerable effort. The group recommended that a task force of ten graduate students, under the leadership of a full-time administrator, collect available information during the summer of 1973.

The project was supported by the (1) U.S. Environmental Protection Agency, (2) National Science Foundation (International Decade for Ocean Exploration), (3) the U.S. Department of Commerce (National Oceanic and Atmospheric Administration), and (4) U.S. Coast Guard. The results of the summer effort were to be evaluated at a workshop in the fall of 1973.

Recruitment of the summer research associates was initiated with a letter from the National Academy of Sciences to oceanographic laboratory directors and department chairmen requesting nominations of pre- and postdoctoral students. Over sixty applicants were considered.

A group met on April 4, 1973(4) to establish guidelines for the study and to select summer research associates. Classes of potential ocean pollutants suggested for study included: hospital wastes, agricultural wastes, litter, synthetic organic chemicals, dumped materials, and transuranic elements. Ten young scientists from ten different organizations were chosen who had strong science or technology backgrounds, high motivation to participate in the project, and excellent recommendations from the faculty of their institutions.

In May 1973(5) a meeting was held with the summer research associates and scientists knowledgeable in the production and ultimate fates of these materials. This meeting reviewed strategies on the examination of transuranics, synthetic organic chemicals, particulates, extractive metallurgy (especially of titanium), hospital wastes, agricultural wastes, and a systems approach. An initial set of materials were proposed for investigation as explained in Chapter 1. All of the participants recognized that certain substances then considered critical would be dropped as the summer progressed, while others, not yet identified, would become apparent. Documentation of the information to be accumulated was emphasized. Much of the information would come from personal communications and records existed only in the files of the correspondent. The importance of collecting all data used was emphasized.

The summer program began on June 1, 1973 at the National Academy of Sciences, Washington, D.C., under the direction of William Robertson IV, with Ms. Laurie A. Goldstein as project secretary. For three months the research associates probed widely-dispersed information sources for pertinent data and some of the committee members visited the group to provide guidance and encouragement. The summer program produced nearly 1200 pages of background reports.

A workshop to review these data was held at the Marine Biological Laboratory, Woods Hole, Massachusetts, between October 29 and November 2, 1973. Its objectives were:

1. To assess and extend our information base and technical ability for handling unanticipated effects of man's products and activities on the marine system.
2. To appraise the method used to accumulate information in the summer study and evaluate the background reports.
3. To predict future effects that might arise from the use of the materials considered and to formulate recommendations for action.

The workshop deliberations, combined with pertinent materials from the background papers, form the basis for this report. The collaboration between the summer associates and the representatives from the scientific and technological community was most effective in refining the background papers into a more concise and substantial presentation. The research associates have been encouraged to publish those materials that do not appear in this publication. The original materials, reprints, books, and other information that formed the basis for the background papers and which are not normally available have been deposited with the National Oceanic Data Center for indexing and storage and will be made available to other investigators.

Edward D. Goldberg,
Study Chairman

NOTES

(1) Participants at 27 July 1972 Meeting: Edward D. Goldberg, Scripps Institution of Oceanography, Chairman; George B. Morgan, U.S. Environmental Protection Agency; Elmer Robinson, Washington State University; William Matthews, Massachusetts Institute of Technology; J. M. Woods, University of Illinois; Adel F. Sarofim, Massachusetts Institute of Technology; C. S. Giam, Texas A & M University; Earl Scott Tucker, Monsanto Industries Chemical Co.; John Bosch, U.S. Environmental Protection Agency; and William Robertson, Richard C. Vetter, and Richard Carpenter, National Academy of Sciences.

(2) Participants at 8 September 1972 Meeting: Goldberg, Chairman; Robinson; Matthews; Sarofim; Giam; Vetter; Robertson; Patrick Parker and Robert Rabin, National Science Foundation; and Richard Hallgren, National Oceanic and Atmospheric Administration.

(3) Participants at 9 January 1973 Meeting: Goldberg, Chairman; Tucker; Giam; Matthews; Sarofim; Robertson; Joseph Perkowski, Massachusetts Institute of Technology; and Mary Hope Katsouros, National Academy of Sciences.

(4) Participants at 4 April 1972 Meeting: Goldberg, Chairman; Matthews; Tucker; Vetter; Robertson; Ian C. T. Nisbet, Massachusetts Audubon Society; and Hugh Thompson, U.S. Environmental Protection Agency.

(5) Participants in Chicago Meeting 11, 12 May 1973: Goldberg, Chairman; Matthews; Robinson; Tucker; Robertson; L. L. Falk, E. I. duPont de Nemours & Co.; William O. Forster, Atomic Energy Commission; John Goldsmith, Department of Public Health, State of California; Robert J. Moolenaar, Dow Chemical, U.S.A.; Theodore Vermeulen, University of California, Berkeley; Frank Viets, U.S. Department of Agriculture; and the ten Research Associates.

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SECTION 1

THE STUDY AND ITS RESULTS

CHAPTER 1

OVERVIEW

PURPOSES

In this study we attempted to develop and test a method for reviewing technologies with a potential impact on marine systems, and to determine whether they clearly pose a potential hazard, whether they are clearly unimportant, or whether they fall into an intermediate category and need further study. In general, marine systems are too complex, and too little is known about their functioning to permit evaluating the impact of all possible technologies on them. We chose to make interim studies of case-histories, guided by experience gained in past crises.

We selected six groups of materials for study. We did not attempt to select cases that represented the full range of marine pollution problems: the primary consideration in selection was the possible availability of sufficient data to permit tentative evaluations of hazard. Nor did we select only cases in which a significant hazard was already suspected: one goal of the study was to determine how a problem could be estimated to be of negligible importance, and some case histories were selected accordingly.

GENERAL RESULTS AND ASSESSMENT

The study proved successful; some definite conclusions resulted despite the limited data and time available for assessment. Detailed assessments are given in Chapters 3-8. We identified two of the materials studied--transuranic elements and hexachlorobenzene--as clear potential problems, at least when the present limited production is projected into the future. We determined that

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a number of the others--low molecular weight chlorinated hydrocarbons (LMCH's), acrylonitrile, iron and copper wastes, open ocean litter, tetracycline, and technetium--present no demonstrable hazard to open ocean ecosystems at present or foreseeable levels of release. Where doubts remained (e.g., on possible effects of LMCH's and tetracycline in inshore waters), the specific information needed to resolve them is identified. In the remaining cases (aromatic hydrocarbons, certain dumped chemicals, and inshore litter) we thought that some local adverse effects were possible, but the area of uncertainty could be narrowed and the information required to determine effects was specified.

In most cases we felt that these tentative conclusions require confirmation by measurements of environmental levels in critical areas together with additional measurements of chronic toxicity to key species. These additional tests are indicated in the respective chapters. However, in most cases only a small number of well-chosen measurements would suffice to resolve the remaining uncertainties. Thus a general conclusion of this study is that many potential ocean pollution problems can be assessed by a detailed review followed by a limited number of well-planned measurements.

KEY CHARACTERISTICS OF POTENTIAL POLLUTANTS

The following parameters recurred repeatedly in our case studies as critical for evaluation of a material's importance:

1. rates of release into the environment;
2. lifetimes in the environment (or residence times in regions where accessible to biological systems);
3. concentration factors in parts of the system (e.g., surface films or estuaries) or into organisms (bio-accumulation); and
4. levels of toxicity.

The propensity for transformation into more hazardous chemical forms, a characteristic proven important in some past pollution problems, was not identified as a factor in any of our cases.

Each of these characteristics may be difficult to assess in certain cases. Information on rates of production or release may be proprietary (e.g., some synthetic chemicals), unknown (e.g., hexachlorobenzene), or secret (e.g., plutonium). Dumped material is often poorly characterized chemically. Estimation of lifetimes in the environment often depends on uncertain extrapolation from laboratory experiments. Estimation of residence times in the ocean also requires knowledge of the timescale for transfer to and from other media (e.g., sediments or atmosphere): the rate-limiting factors for these transfers are little known. Bioaccumulation factors for some chemicals can now be predicted (Chapter 4), but other factors leading to local concentration are less well understood. Similarly, biotransformation is not yet sufficiently understood for prediction of mechanisms or rates. In nearly all the case studies, little or no information was available on chronic toxicity to marine organisms.

EXTRAPOLATION TO OTHER MATERIALS

The methods adopted for this study have proved adequate to yield preliminary assessments of the potential impact of certain materials on the oceans, and to rank them in order of urgency for control measures or for further investigation. We recommend that, with minor modifications, the same methods be applied systematically to other materials. The first stage in this process should be a screening of potential pollutants for those with the key characteristics identified in the previous section. Materials that are persistent and toxic, persistent and bioaccumulated, or persistent and released in large volume, should have high priority for attention. For these priority materials, attempts should be made to estimate distribution and exposure levels in the environment (Chapter 2). Levels that are predicted or measured in the environment should be compared with known or estimated toxic thresholds. For materials identified as potential problems, further investigation will be required, including tests of chronic toxicity, experiments with model ecosystems, and measurements of levels in key areas of the environment. Field studies and monitoring programs would then be required if a significant problem is clearly identified. This study has shown that each material has peculiarities of its own, so it is impossible to reduce this program of assessment to a formula. In addition, it is unlikely that we have discovered the full range of environmental behavior of materials, so that we should be prepared for new surprises and should actively search for new phenomena.

PREDICTING ENVIRONMENTAL TRANSPORT AND EXPOSURE LEVELS

The first task in assessing the potential importance of a material is to estimate the degree of exposure of sensitive organisms. This requires constructing a more or less quantitative transport model to predict levels in the environment from rates of release. The requirements of such a model are outlined in the next chapter, but *two conclusions are worthy of special emphasis.*

1. *It is impossible to construct an adequate model without some data on quantities used and rates of release into the environment.* Where data on production and uses of a material are not available (e.g. because they are commercial or national security secrets) this is a very serious obstacle to assessment of its potential impact. Where data on production are genuinely unknown (as in the case of a toxic by-product such as HCB) assessment requires an expensive program of environmental monitoring.

2. If sufficient data are available on uses and rates of release, *only a few well-chosen measurements are needed* to make the rough estimates of residence times and transport rates for a preliminary assessment of potential impact.

PREDICTING BIOLOGICAL IMPACT

The greatest uncertainty in assessing the impact of ocean pollutants is the scarcity of data on their chronic toxicity as illustrated by the results in Chapter 4. We judged acrylonitrile, generally regarded as hazardous to man because of its high acute toxicity, to be unimportant as a potential ocean pollutant because of its short life in the environment. On the other hand, we judged hexachlorobenzene, hitherto generally ignored as a hazard because of its low volume use, to be a potential hazard in the ocean because of its persistence and the tendency of organisms to accumulate it and thus be chronically exposed to it.

In many of our case-studies, estimates of chronic toxicity had to be extrapolated from measurements on terrestrial or freshwater organisms, or from short-term experiments at relatively high doses. While these measurements give a rough indication of biological activity, their extrapolation to predict chronic effects at low exposure levels is a very uncertain process. This appears to be the case for effects on plankton, for which response does not vary greatly with dose. This indicates the possibility of small effects at extremely low doses. One important research need is for exploration of these effects and for the development of a standard bioassay system.

Even if good experimental data were available on sublethal toxic effects of individual chemicals on representative species, it would be difficult to deduce effects on marine ecosystems. Many plant and animal species reproduce in numbers which exceed those necessary for maintainance of the population, so that a modest reduction in productivity or reproductive rate may have no observable effect on population levels until a certain threshold is reached. Even severe reductions in populations, if sufficiently local, may be replenished rapidly by immigration from neighboring unpolluted areas. Where this replacement does occur there is the danger that the genetic variability of populations may be reduced causing a loss of adaptability in that segment of the species. Population levels in mixed communities may be set by interspecific competition or by selective predation, and a small change in ambient conditions may sometimes lead to large changes in relative population levels. Hence, the same toxic stress may lead in some circumstances to negligible changes in ecosystems, but in other circumstances to large changes. Thus, if a bioassay system in the laboratory is to provide a good guide to the behavior of a real marine ecosystem, it should involve a multispecies community--i.e. a model ecosystem.

Another major problem in interpreting the results of chronic toxicity experiments is the possibility of additive or synergistic effects. If the concentration of a material in the environment is 100 times less than the toxic threshold measured in the laboratory, it is tempting to dismiss it as of no ecological significance. On the other hand, if there are 100 or even 10 different materials present in a natural system at comparable levels of concentration it may be seriously misleading to consider their effects separately. There is an urgent need to conduct experiments to investigate additive or synergistic toxicity of materials. It would be unrealistic to attempt to test all the millions of possible combinations, but it is important to test the effects of combinations similar to those in polluted waters.

A special case is the combined effect of chemical pollution and other stresses, such as predation pressure. Although clear cases are difficult to document, it is expected that chemical pollution would have a much greater effect on populations (e.g. fish) that are being exploited to their replacement limit than on natural stocks that have a reserve of production from which to make good losses. In such circumstances the combined effect of pollution and exploitation might well be to deplete the natural gene pools: this is one of the major concerns of biologists with respect to massive reductions of fisheries' stocks. Recruitment from other areas may lead to rapid restoration of populations, but may also incorporate new, perhaps less favorable, gene combinations into the stock.

Among the most usual effects of human induced stresses on natural ecosystems are reductions in productivity and diversity. Diversity is valued in itself, but is also generally associated with stability in ecosystems. Although the relations between diversity and stability in ecosystems are by no means consistent, they provide the best available measures of stress in natural systems. Since it is usually impracticable to measure changes in population size or productivity in marine organisms, changes in species diversity are often the only evidence that adverse effects may actually be taking place. The natural variability in natural systems is usually high, so that only large changes can be detected with certainty. Determination of diversity changes assumes an ability to make consistently critical identifications of the species involved. Such studies may require more than the present number of trained individuals.

IRREVERSIBILITY

Most effects of toxic materials on ecosystems should be reversible when the toxic stress is removed. However, in some cases, the time scale for recovery may be long. Although these effects are by no means small in terms of human values, there is a special significance to be attached to potentially irreversible effects.

At least two different types of effects of materials should be considered irreversible:

1. Introduction of toxic materials with essentially infinite lifetimes (much longer than a human generation). Plutonium is a prime example among those included in this study.

2. Extinction of locally endemic species, such as coral reef fishes or seabirds confined to single islands. Historically, many cases of extinction of endemic species have been traceable to the introduction of alien competitors, predators, or pathogens. We did not consider this "biological pollution" in this study, but it would be a significant part of any complete program of assessment of human impact on marine systems.

LIMITATIONS OF THE STUDY AND RESEARCH NEEDS

Several limitations of the study, and limits to its extrapolation to other pollutants, have already been pointed out. It is almost impossible to assess the significance of a pollutant without some data on production and releases into the environment. Environmental transport models are limited in precision by a lack of knowledge of critical transfer processes. Very little precise information is available on chronic toxicity to representative organisms, and even less on ecosystem effects.

Particularly lacking are data on additive, synergistic, or antagonistic effects among materials and natural stresses. It is a serious oversimplification to consider the effects of materials separately. Pending better scientific understanding of system behavior, field surveys of affected areas will provide the best evidence for major adverse effects, but are unlikely to reveal subtle ecosystem effects or slow changes.

Another limitation of the study is that we were forced by time and availability of information to consider data largely from the United States, and thus we were generally restricted to considering effects of U.S. technology on adjacent marine systems. Some of our conclusions could be extended to other parts of the world. However, other countries have different disposal practices, and the biological characteristics of other oceans are demonstrably different, so this extension should be made with caution. Collecting data for a global survey of oceanic pollution would be a difficult task, because of the necessity of obtaining data on uses and releases. One of the materials included in this study--plutonium--appears to be of truly global significance. Only a few other materials may fall into this category. Global studies, although difficult and expensive, should not be impracticable.

OBSERVATIONS

The transuranic elements are of great concern because of their high toxicity, long life, and increasing production with increased risk of loss to the environment. Marine problems with transuranics are likely to originate in a relatively few areas determined by the locations of nuclear reactors, fuel reprocessing plants, and radioactive materials transportation routes. The primary concern is to establish and maintain the most rigorous housekeeping and monitoring programs possible.

The increasing role of synthetic organic chemicals in our society will almost inevitably result in increased levels of these compounds in the environment. The mass flow type of estimates, as developed in this report, are essential to predicting exposure levels for all parts of the environment. It is not possible to construct these estimates or to assess potential effects without complete and accurate production and use data. Methods should be devised for making these data available while protecting the legitimate interests of private industry. Where the data were available we have made predictions which can and should be tested by a few measurements in identified areas of the marine environment. Priority attention should be given to synthetic chemicals with one or more of the following characteristics: high-volume production, long life, high toxicity, localized discharge, or bioaccumulation potential.

The descriptions of waste materials and of dumping sites in EPA permits are far too vague to permit assessments of potential effects of their discharge to the oceans. Accurate and complete data on the composition of materials to be discharged and on the discharge sites are essential. Discharging any type of waste into biologically productive areas seems particularly imprudent with our lack of basic knowledge. The disposal of dredge spoil is unnecessarily complicated by the introduction of contaminants. With maintenance dredging cycles of 1 to 5 years common throughout the U.S., careful control of the source of contamination could virtually eliminate this problem in a relatively short time.

Generally, the disposal of metallic wastes in the oceans will result in small changes in already large background concentrations on a global basis. We cannot evaluate the natural variability of metals in the oceans or predict how much of a dislocation will have any given effect. However, it is important to note that relatively large injections of toxic metals to relatively confined or restricted ocean areas may have pronounced effects.

Tetracyclines and technetium-99 are our case studies in medicinal wastes. The former collection of substances is not likely to be found in biologically active forms in the marine environment. The short half-life of Tc-99 and the present production rates indicate that potentially dangerous amounts will not be transported to the oceans. For tetracyclines a possibility exists that very low levels could spur development of resistant pathogenic strains of microorganisms. These conclusions are made in the absence of marine data. A relatively few measurements of these materials, for example tetracylcines in the New York Bight sludge disposal area and technetium-99m in Boston Harbor, could verify or refute the conclusions. Extensive sampling or monitoring programs are not warranted.

Using our estimates of litter generation and the data on effects, we could not identify ecologically significant alterations in the marine environment caused by litter. However, there may be deleterious effects in regions of litter accumulation. The primary impact of marine litter at this time appears to be aesthetic. The U.S. could be the source of one-third of the total world marine litter, based on correlations with gross national product.

RECOMMENDATIONS

- The mass flow estimate technique outlined in Chapter 2 should be systematically applied to materials used or created by human technology.

- The rapidly increasing production of transuranic elements, combined with their present and potential leakages to the environment, could lead to concentrations in the environment that, because of the toxicity of these elements, would jeopardize the health of man and the integrity of ecosystems. Releases of transuranic elements to the marine environment should be kept to an absolute minimum. Any releases should be monitored, and plans for significant increases above current levels should be carefully scrutinized and regulated. For any release of transuranic material, the rate of release, amount, nature, and composition of the material, and the pathways of the material in the environment should be studied. Mass flow estimates should be prepared for all pathways and materials. The current hazard assessment models for container-dumped transuranic elements should be reevaluated and should include determination of container life and location, matrix life, and leach rates, as well as mass flow and effect estimates for the released transuranic elements. The worldwide proliferation of nuclear power plants makes the cooperation of many governments essential in the control of this material.

- Increased use of low molecular weight-chlorinated hydrocarbons will result in increased levels of these compounds in the environment. To predict future exposure levels for the oceans and the atmosphere, and to understand present-day dispositions more clearly, mass flow estimates (outlined in Chapter 2) should be formulated and checked by measurements of the substances in rivers and sewer effluents, as well as in the ocean and atmosphere. It must be emphasized that production and use data are essential to such assessments. At present, it is often impossible to obtain these data.

- Wastes should not be discharged into biologically active marine areas. Data on biological, physical, and chemical characteristics of any materials proposed for discharge, and of nearshore ocean areas, should be obtained. Insufficient data are now available for the proper evaluation of proposed discharges. Most waterways in the U.S. have a maintenance dredging cycle of 1 to 5 years, and the quality of the dredge spoil is directly related to the contaminants introduced to the dredged waterways. We recommend that the sources of these contaminants be eliminated.

CHAPTER 2

GENERAL METHODS FOR SCREENING POLLUTANTS

On the basis of the experience gained in this study, we propose that evaluations of the potential hazard posed by materials to the ocean system should be carried out in three or four stages. The first--primarily a mail-and-telephone exercise--is a screening of materials in production to determine which ones merit consideration. The term "materials" is used in a broad sense in this chapter: this method is applicable to materials poorly characterized chemically, such as litter, dredge spoil, chemical waste, mine tailings, or radiological or biological materials. The most important criteria to be used in this evaluation should be: (1) the quantities and forms produced, used, and dispersed; (2) persistence; (3) bioaccumulation; and (4) toxicity. If not known precisely, the quantities dispersed must be estimated from the known or expected uses. In some cases, the other three characteristics will have been measured; in some cases they can be extrapolated from similar chemicals; in other cases, they can be at least guessed from such chemical characteristics as composition, molecular structure, and activity relationships.

For those materials selected for study, the second stage in evaluation is to make a rough comparison of expected levels in the ocean with dose-response data. We assume that some information on toxicity will be available for each material so that chronic toxicity can be at least estimated by analogy with well-studied materials. Estimation of exposure levels requires construction of a crude transport estimate. The information needed for this estimate is discussed in the following sections. To be convincing, a transport estimate requires verification through actual measurement of environmental levels. The important point is that relatively few measurements are required to give the essential information necessary at this stage. Half a dozen numbers for measurements of concentrations in air and water in areas remote from sources coupled with estimates of releases may suffice to give an order of magnitude estimate of residence times and dispersion in the atmosphere and oceans. In many cases, this is all that is necessary to show whether toxic thresholds are likely to be approached.

The third stage in evaluation will be appropriate only for the more toxic or persistent materials--those in which predicted or measured concentrations fall within a factor of 100 (p. 8) of estimated levels of concern. For these materials, a more refined transport estimate should be developed, in conjunction with sufficient measurements to establish residence times and critical pathways through the marine system. At the same time, chronic toxicities to representative organisms at appropriate levels should be measured. To represent adequately the conditions of exposure that actually occur in the marine environment, it is necessary to take into account additive, synergistic, and antagonistic effects with other pollutants and natural stresses and to measure effects on communities in model ecosystems. This third stage is essentially a research function in which the full analytical and toxicological expertise of specialized laboratories must be used.

ENVIRONMENTAL TRANSPORT ESTIMATES

General Consideration

One purpose of studying individual materials, as undertaken in this report, is to develop a general approach that can be applied to other potential pollutants in the future. The question to be asked in such studies is whether a particular substance may cause adverse effects after release into the environment. To answer this question requires comparison of dose-response data with the levels predicted or measured in the environment. To determine the dose-response relationships it is necessary to conduct toxicological tests with representative test species at appropriate exposure levels. To determine environmental levels it is necessary to construct an environmental transport estimate which will relate quantitatively the emissions of the substance into the environment to its subsequent movement, accumulation, and fate in various compartments of the environment. An environmental transport estimate has three main functions: (a) to relate environmental levels to specific inputs, so that the effects can be predicted; (b) to identify critical transfer processes and gaps in knowledge, so that environmental monitoring can be planned for maximum efficiency; (c) to predict locally high exposures, so that appropriate toxicological studies or field surveys can be carried out.

The first stage in constructing an environmental transport estimate will generally be quite crude. The example given in the section on low molecular weight chlorinated hydrocarbons (Chapter 4) shows how a calculation to order of magnitude only can suggest critical pathways and indicate the importance of minor inputs into the environment. In the first stage the continental or global environment can be considered in four compartments--land, freshwaters, ocean, and atmosphere. Spatial gradients within the compartments will be predicted if residence times are short compared with the times for spatial movement; alternatively, if spatial gradients are found, this will provide information about the relative magnitudes of these time scales. Detailed estimates for sensitive areas, such as estuaries, can be constructed at a later stage.

In principle, an estimate could be used to predict levels in the environment, given enough information on rates and locations of release and on rates and routes of transfer. In practice, however, the information available initially includes some sketchy information on levels in the environment together with incomplete information on uses: the estimate is then built from both ends in order to deduce those pathways through the marine system. Checks for consistency and plausibility, and analogies with substances studied earlier, are important elements at this first stage in development.

Despite the wide variations in the behavior of materials in the environment, the same basic items of information on each substance are required for constructing estimates.

Production and Uses

Figures on production are available for many substances. It is almost impossible to construct adequate estimates for substances for which these data are not available. Use figures are often more difficult to obtain and may require innovative guesswork. Uses must be classified according to the potential for release: minor uses occasionally represent significant sources, so that it is necessary to review all the potential uses of a substance, including secondary manufacturing which may not be recorded in standard source books.

Rates of increase in production or use are significant for predicting future impacts, or interpreting past changes.

Rates of Emission

Rates of loss into the environment should be classified according to the compartment into which the chemical is originally released:

1. Atmosphere -- direct release (propellants, gases, volatile liquids); evaporation (solvents, plasticizers); dispersive uses of liquids or solids (pesticide sprays, fire extinguishers, cloud seeding); gaseous by-products (e.g. CO, SO_2); production losses of volatile materials.

2. Freshwaters -- production losses of liquid materials; disposal of used liquids into drains; spills in river and lake transportation. These emissions are usually very hard to estimate: monitoring of sewage effluents or concentrations in rivers often provides the best information.

3. Land -- disposal of domestic and industrial wastes. Precise information on the composition of solid wastes is usually hard to obtain: the best estimates are often derived from estimates of working life of manufactured objects and from information on disposal practices.

4. Ocean -- industrial dumping; dumping of dredge spoils; direct discharge through outfalls; marine uses (e.g. paints, lubricants). The EPA permit system for ocean dumping offers prospects for obtaining better information on industrial wastes, but the contents of dredge spoils and ship-generated wastes are very difficult to determine at present.

Verification of Estimates

In principle, a predictive estimate should be tested by independent observation of concentrations and gradients in the environment. In practice, however, most estimates are based on inadequate knowledge of emissions and environmental distribution is incorporated into the estimate at a very early stage. The first crude estimate then suggests new measurements to make, and these usually lead to modification of the estimate. Prediction and verification are achievable goals although no estimates have yet been subjected to rigorous evaluation.

Information Required

To predict the behavior of a previously unstudied substance, the following items of information are usually required: production and use data; vapor pressure as a function of temperature, vapor density; solubility in water and organic solvents; partition coefficients between water and lipids, between water and particles, and between air and particles; chemical reactivity in the presence of UV light, oxidants, and H_2O; chemical transformation in relation to pH; micorbial decay under aerobic and anaerobic conditions; residence time in different environmental compartments. The behavior of a substance in a model ecosystem may be a helpful guide to its behavior in the natural environment.

Critical Areas of Ignorance

Several mechanisms of environmental transfer that have been identified in some modeling studies as being critical pathways are nevertheless very poorly understood. The following mechanisms have high priority for future research:

1. Losses from dumps -- Many synthetic substances are believed to have accumulated in dumps, often buried in landfills. It is not known whether they will remain there permanently or whether some of them will be released slowly in the future. Information is needed on the potential for vaporization or leaching from dumps.

2. River transport -- Models are available for the transport of sediments in rivers in regular and

irregular flow conditions. The rate of transport of substances in rivers depends not only on the flow of dissolved and suspended material, but also on the kinetics of sorption and desorption on particulates, diffusion in sediments, uptake by biota, and chemical reactions such as flocculation and precipitation.

3. Sedimentation and resuspension -- Heavy hydrophobic chemicals such as PCB's and HCB may be strongly adsorbed onto particulate matter and concentrated in sediments. Sedimentation in the deep ocean probably represents an ultimate removal of these materials from the human environment. It is not clear to what extent sediments in the shallow sea represent a sink for these substances or merely a temporary storage site from which they will be released slowly in the future.

4. Degradation in the atmosphere -- Photochemical degradation and hydrolysis are critical pathways of loss for some materials, but their rates depend on altitude and on the presence of substances such as dust particles, NO, and H_2O. It is not known to what extent these reactions are rate-limited by the concentrations of these other substances or by the rates of upward diffusion.

5. Ocean surface phenomena -- Rates of transfer across the ocean surface may be influenced by turbulent diffusion in the upper layers, by adsorption on particles, and by the presence of surface slicks. The extent to which materials may be concentrated into surface layers or transferred to the atmosphere in spray needs detailed study.

6. Adsorption onto particles -- The partition of materials between particles and the vapor or liquid phases may determine rates of transfer, but has been little studied.

7. Food webs -- The movements of materials within marine food webs are generally not understood.

Transport and Transformation in the Environment

After release into the environment, materials may be transported to other areas or transferred to other media in many different ways. The following processes all need to be considered, although in many cases only a few will be found to be significant:

1. Processes in the atmosphere
    - a. Transport of vapor-phase material by wind
    - b. Transport of or on particles by wind
    - c. Vertical diffusion (important if there is a high-altitude sink or low-altitude transfers to other media)
    - d. Fall-out and dry-deposition of particles
    - e. Rain-out of particles
    - f. Solution of vapor in the ocean
    - g. Chemical changes such as photochemical oxidation and hydrolysis (both may depend strongly on altitude and on the presence of other chemical species)
2. Processes on land
    - a. Diffusion into soil as vapor or in water solution
    - b. Volatilization from soil by vaporization or by steam or wick distillation
    - c. Volatilization from burning dumps, incinerators or reprocessing plants
    - d. Leaching into groundwater
    - e. Adsorption and desorption from soil particles
    - f. Wind or water erosion of soil particles
    - g. Metabolism by soil organisms
    - h. Uptake by plants and animals
3. Processes in freshwater
    - a. Chemical transformations, including precipitation
    - b. Adsorption and desorption from suspended particles or sediments
    - c. Transport on sediments
    - d. Resuspension and transport of shallow-water sediments such as occurs in estuaries or during storms

  e. Diffusion into sediments
  f. Evaporation from surfaces
  g. Distribution of water and its contaminants by irrigation can be locally important for predicting human exposure
  h. Uptake and metabolism by plants and animals

4. Processes in the ocean

  a. Chemical transformations, including precipitation
  b. Adsorption and desorption from suspended particles or sediments
  c. Sedimentation of suspended particles
  d. Resuspension and transport of shallow-water sediments such as occurs in estuaries or during storms
  e. Diffusion into sediments
  f. Uptake and metabolism by plants and animals
  g. Transport in ocean currents
  h. Vertical mixing and diffusion in upper layers
  i. Concentration in surface films
  j. Evaporation or ejection in spray

Bioaccumulation

An evaluation of the potential for bioaccumulation and bioconcentration in food chains is critical for assessing the exposure of predatory animals, including man, but usually is of negligible importance for assessing mass flows. Bioaccumulation of lipophilic chemicals is now reasonably well understood and predictable (Chapter 4). However, bioaccumulation of protein-bound substances such as heavy metals is less well studied.

Assessing Time Scales

With an abundance of possible pathways for transport and transfer between media, the first task in developing a crude transport estimate is to determine the critical pathways for each substance. To a first approximation, the mass flow estimate for the quantity of a substance in any compartment of the environment equals the sum of the inflows minus the outflows. In this context, degradation and transformation are considered outflows. In some cases the substance may have reached an approximation steady-state distribution in which the inflows approximately equal the outflows. The controlling factor is the fastest outflow and accordingly the first task is to seek the transfer process with the shortest time scale.

The time scales for some processes (e.g. atmospheric and oceanic transport or mixing) may be known for more than an order of magnitude; others can be measured in the laboratory for specific substances (e.g. evaporation from solution or soils); others can be estimated from sample measurements (e.g. measurements of river flow and concentrations in water). Time scales for some processes are difficult to estimate; however, photolysis and biodegradation, for example, can be simulated in the laboratory, but it is difficult to be confident that the experiments adequately represent the processes actually occurring in the environment. In some cases search for breakdown products may be the best way to estimate rates of loss.

When the process with the shortest time scale has been preliminarily identified, it should be checked for consistency with measurements of environmental levels. A relatively few representative measurements can be used to derive an estimate of the total quantities in the atmosphere or the ocean: comparing this with rates of emission gives an order of magnitude estimate of residence time. If this estimated residence time is substantially less than the time scale of the most rapid known transfer process, a more rapid route of loss must be identified.

Residence time may also be estimated from observations of spatial gradients. If a substance has been released for a long enough time period to have potentially reached a steady-state concentration, but is actually distributed nonuniformly in the ocean, its residence time must be shorter than the mixing time of the water mass being considered.

Directions of Transfer

Most intermedia transfers can take place in either direction: for example, transfer between ocean and atmosphere can be either upwards, by evaporation, or downwards, by fall-out or solution. Comparison of measured concentrations in the two media can be used to test the hypothesis that the concentrations are in equilibrium; if not, they can indicate the direction of the net transfer.

Spatial Transport

Once the dominant processes of transfer between media and of ultimate loss have been identified, it is necessary to make more detailed estimates of each environmental compartment. These estimates will relate diffusion and transport within the compartment to rates and locations of input. The goal of this exercise is to predict spatial gradients and rates of change of concentration.

CONCLUSION

We propose these methods for assessing potential ocean pollutants as a step forward in our efforts to live productively within our environment. The time when we could afford to stumble from crisis to crisis has passed and we must begin to anticipate our impacts on the oceans and the environment. As knowledge and understanding increase, our methods for screening pollutants should evolve and improve. The method described here is by no means perfect. However, we must not put off developing the type of capability described here.

SECTION II

CASE STUDIES

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CHAPTER 3

TRANSURANIC ELEMENTS

Workshop Panel

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Background Paper

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INTRODUCTION

We considered transuranic elements as possible contaminants in the marine environment because of their extreme toxicity, potential harmful effects to marine plants and animals, and subsequent danger to humans through ingestion of seafood. Although very small amounts of many transuranics must exist in nature as the result of constant interaction of ^{235}U and ^{238}U with environmental neutrons, only in pitchblendes of high uranium content have any of these nuclides been found in measurable amounts. In the normal environment, all transuranics may be assumed to be man-made. By 1970, the release of over 200 x 10^5 kilocuries of alpha-emitting plutonium into the oceans as fallout (Hardy *et al.* 1973) had resulted in plutonium contamination of marine organisms throughout the world. Transuranic nuclides entering the marine environment either remain suspended in the water, become sorbed to the surface of biota and detritus, incorporated in the tissues of organisms, or associated with

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the sediments. Oceanic areas with high biogenic sedimentation rates might act as sinks for plutonium and other transuranic nuclides.

The transuranic elements are those with atomic numbers greater than that of uranium; all of their nuclides are radioactive decaying with the emission of either a beta or an alpha particle, frequently accompanied by the emission of one or more gamma rays. In addition, many of these elements undergo spontaneous fission, emitting neutrons and producing two or more elements with lesser mass. Because of the similarities of the alpha particle energies of ^{239}Pu and ^{240}Pu, they are not now analytically separable by alpha spectrometry; therefore all references to ^{239}Pu will include ^{240}Pu unless otherwise specified. Due to their short half-lives and limited availabilities, elements with atomic numbers greater than 99 probably will not provide a significant source for marine effects in the immediate future. To date, research pertinent to this report has been almost exclusively concerned with ^{238}Pu, ^{239}Pu, and ^{241}Am, all long-lived radionuclides of high toxicity, which pose a continuing hazard when introduced to the marine environment.

The rate of plutonium 239 production in conventional light water reactors (LWR) today amounts to twenty-three curies per MWE (megawatt electrical) year of operation (Stockholm International Peace Research Institute, hereinafter referred to as SIPRI, 1972). On an activity basis only ^{239}Np and ^{241}Am are produced in LWR fuels in lesser amounts than ^{239}Pu. In proportion to ^{239}Pu, liquid-metal fast breeder reactors (LMFBR) will produce less of all of the transuranics considered except for ^{239}Np, although in absolute terms, most will be produced at higher levels. The primary peacetime uses of transuranics are as fuels in power reactors, but they also find use as energy sources for satellites and medical devices. However, the largest inventory of transuranic elements is in nuclear weapons.

Transuranics have high toxicity, and they will increase in amount; therefore, we urge that great care be exercised in minimizing any release of these substances to the environment. Because of the possible differences in their behavior in the marine environment as compared to more generally studied systems, investigations are needed to evaluate their total present and future effect. We have suggested several investigations and control measures.

While introduction of transuranics to date to the marine environment has not resulted in known hazardous exposure to humans, it cannot be assumed that there have been no effects on marine organisms.

CHEMICAL AND PHYSICAL CHARACTERISTICS

There are extensive bibliographies covering the chemical and physical laboratory behavior of the actinides, those elements in the periodic chart which, like all of the transuranic elements, have partially-filled 5f orbitals and which show a number of different chemical properties, under varying conditions, similar to the aqueous behavior of the 4f lanthanide elements (Seaborg and Katz 1954, Seaborg 1963, Wick 1967).

Several variables in the marine environment (ionic composition, redox potential, pH, temperature, pressure, the presence of complexing agents) govern actinide chemistry (Polzer 1971). Advantage may be taken of the slight changes in response to these variables to separate one element from another (Bentley *et al.* 1971, Bishop *et al.* 1971). Table 3-1 shows the variety of oxidation states for the 5f transuranics of concern.

TABLE 3-1

Oxidation State and Stability of Selected Transuranic Elements

Element	Oxidation States (most stable underlined)	Most Stable Form in Air and Water
$_{93}$Np	3,4,$\underline{5}$,6	NpO_2^{+1}
$_{94}$Pu	3,$\underline{4}$,5,6	Pu^{+4}, PuO_2^{+1}
$_{95}$Am	$\underline{3}$,4,5,6	Am^{+3}
$_{96}$Cm	$\underline{3}$,4	Cm^{+3}

The transuranics have a strong tendency to form colloids or polymers in aqueous solution. Such a tendency favors removal from the water column either by sorption to particles with subsequent settling or by biological processes (Kubose *et al.* 1967). In either case, surface-injected transuranics ultimately reach the benthic ocean environment.

Thus, there is considerable geochemical and biological cleansing of various forms of transuranics from surface waters, and the rate of this cleansing should be a function of several variables, such as ionic strength, available complexing agents, surface charges, and redox potential (Andelman and Rozzell 1970). Much of the data accumulated to date on the behavior of transuranics have been gathered without measurement of these important variables. We recommend that future research relative to the marine behavior of transuranics be approached with careful consideration of such variables.

Differences in chemical behavior caused by differences in mass among the isotopes of individual transuranics have not been expected in the environment. However, isotopes with significantly different rates of radioactive decay and specific activity do sometimes exhibit real differences in geochemical and biological behavior. These differences may be caused by the increased enthalpy produced by the heat of reaction incident to the decay. One observed instance of this effect is the difference in relative mobility of ^{238}Pu and ^{239}Pu in organisms and soils (Ballou *et al.* 1967, Johnson 1972, Morin *et al.* 1972). These observations may be explained by the existence, in polymeric forms, of a higher proportion of the nuclide with the lower specific activity.

Therefore, it is not always possible to extrapolate data gathered from one nuclide to predict the behavior of another nuclide of the same transuranic element. Table 3-2 lists the decay characteristics of the transuranics considered, illustrating that the specific activities of the alpha emitters vary over seven orders of magnitude. It is clear that in considering published information on the behavior of any particular isotope, we must consider specific activities before generalizations can be made for other isotopes.

TABLE 3-2

Decay Characteristics of Some Transuranic Nuclides

Element	Nuclide Mass	Half-life (years)	Specific Activity (Ci/gm)	Emitted Particle	Energies of Principal Particles (MeV)
Neptunium	237	2.14×10^6	7.07×10^{-4}	Alpha	4.79, 4.77
	239	1.5×10^{-2}	1.00×10^5	Beta minus	0.43, 0.33
Plutonium	236	2.85	5.34×10^2	Alpha	5.77, 5.72
	238	8.78×10	1.72×10	Alpha	5.50, 5.46
	239	2.44×10^4	6.14×10^{-2}	Alpha	5.16, 5.14
	240	6.54×10^3	2.38×10^{-1}	Alpha	5.17, 5.12
	241	1.5×10	1.00×10^2	Beta minus (99%)	0.021
				Alpha (0.0023%)	4.90, 4.85
	242	3.87×10^5	3.84×10^{-3}	Alpha	4.90, 4.86
Americium	241	4.33×10^2	3.45	Alpha	5.54, 5.49
	243	7.37×10^3	2.02×10^{-1}	Alpha	5.28, 5.23
Curium	242	2.2×10^{-1}	6.83×10^3	Alpha	6.11, 6.07
	244	1.79×10	8.28×10	Alpha	5.81, 5.76

Note: A curie (Ci) is a unit of radioactivity equal to 3.700×10^{10} disintegrations per second.

TOXICITY

Biomedical aspects of plutonium have been studied relatively thoroughly in higher organisms (International Commission on Radiological Protection, hereinafter referred to as ICRP, 1972; Bair *et al.* 1973; Stannard 1973a, b; Vaughan *et al.* 1973). Until recently, the transplutonics have also been studied, though to a lesser degree (Hanford Biology Symposium 1972, Durbin 1973). Work with lower organisms, especially those characteristic of the marine environment, has been less thorough, and there are only a small amount of data available.

We found no conclusive evidence indicating chemical toxicity of transuranics to organisms. The biological effects of the transuranic elements are probably caused entirely by the release of ionizing radiation, predominantly alpha particles. It has been repeatedly demonstrated that alpha particle irradiation is especially effective in producing long-term biological effects. For these reasons, and because of a tendency for long retention periods after absorption, the transuranic elements are frequently considered to be among the most toxic agents known to man (Hanford Biological Symposium 1972, ICRP 1972, Stannard 1973a,b).

The primary, although not the only, biological effect to be considered in higher organisms, including man, is the induction of cancer. Plutonium is remarkably effective in producing osteogenic sarcoma and bronchogenic carcinoma, the type depending largely upon the route of entry of the nuclide (Stover and Jee 1972, Bair *et al.* 1973, Vaughan *et al.* 1973). Some of the other transuranics equal plutonium in carcinogenic potential but rarely exceed it insofar as the present data can be used (Durbin 1973). Most are considerably less effective on a microcurie basis.

Since some of the transplutonics irradiate soft tissue to a greater extent than does plutonium, it is possible that biological effects other than carcinogenesis may play an important role with that group (Durbin 1973). For example, based on time after injection, ^{241}Am seems to be lethal sooner than ^{239}Pu because of its greater accumulated radiation dose in soft tissues. Cases of liver and kidney failure have been recorded. Other effects, including the production of genetic defects, could assume importance at lower dose levels. However, the probability of any of these other effects occurring from environmental contamination is low, and special circumstances such as very widespread distribution would be required to replace the induction of cancer as the controlling biological concern in higher organisms. Other effects may take precedence in lower organisms, but few details can be provided at present.

Once these elements are in the body their solubility is relatively low and absorption poor (ICRP 1972). The absorption from the gastrointestinal tract of ^{239}Pu (in the insoluble form usually encountered) averages only about 3×10^{-3} to 10^{-4} percent of the entering amount. This average may rise by a factor approaching 100 for absorption from the very young (immature) gut or when very soluble forms are administered (e.g., the citrate complexes).

The transplutonics are somewhat more mobile than plutonium and are absorbed more easily. Yet, in work so far performed, it is only in the form of a diethylenetriaminepentacetic acid (DTPA), or ethylenediaminetetracetic acid (EDTA), or a similar complex that gut absorption reaches more than 1 percent. This type of absorption is always of relatively low magnitude, and since this is the most likely route of entry to man from contamination of the oceanic environment, there is a large discrimination factor to counter the high toxicity of the transuranics as a class. Only by inhalation of contaminated particles is the amount absorbed and retained in the body of the order seen for gut absorption of nuclides in the fission product series such as strontium or cesium.

Inhalation seems, in general, an unlikely route of transfer from the marine environment to man. Local instances such as prolonged inhalation of relatively highly contaminated sea spray or dust from dried accumulations on contaminated vegetation should be investigated before the inhalation route is dismissed.

The maximum permissible body burden in man for occupational exposure to ^{239}Pu is 16 nCi (0.3 μg) when the lung is the critical organ, and 40 NCi (0.7 μg) when bone is the critical organ. The figures for americium and curium isotopes are in the same range. Although these are very small quantities, the values viewed as permissible for populations will surely be considerably lower. Despite the large factors discriminating against absorption from the gastrointestinal tract, significant increases in amounts in the environment could lead to organ concentrations approaching the limiting figures. If we add to this the possible substitution of more soluble compounds for those currently encountered and the possibility of greater mobility in seawater as compared to freshwater, the potential for harm from transuranic nuclides accumulating in the marine environment cannot be dismissed. In addition, the amount of the more readily transportable transplutonics (e.g., ^{241}Am) and of the higher specific activity plutonium isotopes (e.g., ^{238}Pu and ^{241}Pu) can be expected to increase significantly over the next three decades. The toxicity of some of these transplutonics approaches that of ^{239}Pu, and even exceeds it under some conditions. Their contribution to ambient levels of radioactivity may increase considerably with time. Thus, the principal reason for concern over the toxicity of transuranics remains the very large increase in total amounts potentially available and the possibility, however small, of release of any appreciable fraction to the environment.

As we have already stated, the heavy elements, including the transuranics, exhibit a tendency to form aggregates at physiological pH's and at those of seawater. This tendency reflects, in part, the insolubility of most inorganic compounds of these nuclides, but the phenomena may occur also when they are complexed with organic moieties. These aggregates may contain hundreds of atoms and are frequently referred to as 'hot spots.' An important unresolved problem in the toxicity of the transuranics is the biological significance of these point sources of activity. Because of the high activities associated with these aggregates, only a few micrometer-sized particles of high specific activity may produce a dose rate considerably above the maximum permissible dose rate. The significance of this possibility depends upon whether or not the high local doses simply kill the cells surrounding the point source or initiate neoplasia or other long-term effects. Conventional radiation dosimetry contributes little to hazard evaluation under these circumstances (Richmond *et al.* 1968, 1970). Research in this area has been somewhat neglected. These phenomena can probably occur in marine environments as well and deserve more study than they currently receive.

Because of their relatively low solubility, it seems unlikely that effects of transuranics would appear in other organisms which would be critical enough to necessitate controls on release rates more stringent than those designed to protect human populations or the evaluation of their consequences. However, the amount of information available to support this conclusion is very inadequate. Thus, the anthropocentric approach must be regarded only as an expedient for lack of information to the contrary. What we need to know now, primarily, is whether there are idiosyncratic events of special pertinence to the marine environment. Until we know this, the present information on toxicity will have to prevail and the transuranics must be considered as potentially very dangerous.

SOURCES

Transuranics are at present, and will continue to be, employed chiefly as fuel for the generation of energy in nuclear weapons, nuclear power reactors, and radioisotope power generators. Other applications of lesser importance have been in industrial measuring devices and gauges, in neutron sources used for mineral exploration, and in medical radiography.

Weapons Testing - Fallout

Fallout from nuclear weapons tests in the atmosphere is the largest source of transuranics to the environment. Accounting for the geographical distribution of the tests, we estimate that 2×10^5 Ci of ^{239}Pu and 5×10^3 Ci of ^{238}Pu have been introduced to the world oceans from nuclear weapons tests through 1970 (Table 3-3). A critical assumption is that atmospheric testing of nuclear weapons will continue at an indeterminable but presumably diminished rate. Therefore, a continuing global source of plutonium through atmospheric testing is anticipated.

TABLE 3-3

Plutonium Delivery to the Earth's Surface (1971)(kCi)

Region	Weapon Tests Pu^{239}	Weapon Tests Pu^{238}	SNAP-9A Pu^{238}
Northern Hemisphere			
Land	105	2.4	1.2
Ocean	155	3.6	1.8
Southern Hemisphere			
Land	14	0.4	2
Ocean	56	1.6	9
Total			
Land	119	2.8	3.2
Ocean	211	5.2	10.8

Source: Volchok 1973, pers. comm.

The inventory of ^{239}Pu in the weapons systems of those countries possessing nuclear armaments probably approaches 10^7 Ci, more than half of which is held by the U.S. (SIPRI 1972, Jane's Weapons Systems 1972, Aviation Week and Space Technology 1973, Washington Post 1973). The geographical distribution of these bombs, missiles, and other tactical weapons is not known. Accidents involving the release of plutonium from U.S. nuclear weapons have been documented (Leitenberg 1970), and the impact of one such incident on the marine environment off the coast of Greenland is described later. We did not attempt to make a projection of the incidence of such accidents, acknowledging the probability that such will occur with an indeterminable frequency.

Civilian Nuclear Power Generation

Growth of nuclear power in response to the mounting demand for energy throughout the world seems inevitable. Many projections of future power needs and the part to be played by the nuclear reactor have been described (Table 3-4). While ^{239}Pu is the principal product in civilian plutonium reactors, other transuranic nuclides will be produced in increasing amounts as time in the reactor is increased. The relative amounts will depend upon the composition of the original fuel and the actual time spent in the core of the reactor. Table 3-5 illustrates a typical transuranic content of spent fuel and is shown as an example of the relative activities expected for the two cases of the light water reactor (LWR) and the liquid metal fast breeder reactor (LMFBR). Spent fuels present more complicated problems than those encountered in plutonium production because of the presence of these other transuranics.

TABLE 3-4

Cumulative ^{239}Pu Production from Nonmilitary Nuclear Power in 10^6 Ci (Metric Tons in Parentheses)[1]

	1980	1990	2000
U.S.	3 (49)	14 (230)	35 (570)
Foreign	4 (65)	20 (330)	59 (960)
World	7 (114)	34 (560)	94 (1,530)

[1] (10^6 Ci)(16.28) = tons.)

Source: U.S. Atomic Energy Commission 1972, SIPRI 1972.

TABLE 3-5

Examples of Transuranic Activities of Spent Nuclear Fuels (Activity Relative to ^{239}Pu)

Isotope	LWR	LMFBR
^{239}Np (β)	.05	2.0
^{238}Pu (α)	8.5	3.2
^{239}Pu (α)	1.*	1.*
^{240}Pu (α)	1.5	1.2
^{241}Pu (β)	350.	70.
^{241}Am (α)	0.6	0.5
^{242}Cm (α)	45.	19.
^{244}Cm (α)	7.5	0.4

* The ^{239}Pu content in the spent fuel of a typical 1000 Mw (e) LWR and LMFBR would be about 10^4 CI respectively.

Source: U.S. Atomic Energy Commission 1971.

The quantity and variety of the transuranic radionuclides present in spent fuel illustrate the magnitude of even potential fractional releases to the environment through handling in the nuclear fuel cycle. Reprocessing of spent fuel results in the transfer of much of these transuranics to long-term storage tanks along with other liquid wastes to be converted eventually to solid form. Table 3-6 gives our estimate of the accumulated transuranics in these wastes by the Year 2000. The recovered plutonium from these operations will be shipped to fabrication facilities for use as fuel. Table 3-7 is our estimate of the quantities of Pu in the stages of the uranium fuel cycle from fuel fabrication to waste storage where there are potential unexpected releases of transuranics. An example of such a potential is the recent leakage of wastes at the Hanford waste storage site

TABLE 3-6

Estimated Accumulated Transuranic Isotopes in High-Level Waste Storage Tanks in the United States from Civilian Sources in the Year 2000

Isotope	Curies
^{237}Np	7×10^4
^{239}Np	7×10^6
^{236}Pu	6×10^3
^{238}Pu	2×10^8
^{239}Pu	7×10^5
^{240}Pu	3×10^6
^{241}Pu	2×10^8
^{242}Pu	7×10^3
^{241}Am	6×10^7
^{242}Am	5×10^6
^{243}Am	7×10^6
^{242}Cm	3×10^8
^{243}Cm	1×10^6
^{244}Cm	9×10^8
^{245}Cm	3×10^5
^{246}Cm	5×10^4

Source: U.S. Atomic Energy Commission 1972.

TABLE 3-7

Estimated Annual Quantities of Pu in the U.S. in Selected Transportation Modes

Category	1980		1990		2000	
	Ci	Tons	Ci	Tons	Ci	Tons
In shipment from inventory for fabrication	0	0	9×10^5	15	6×10^6	100
Spent fuel in shipment to reprocessing	5×10^5	7	2×10^6	33	1×10^7	160
Reprocessed wastes in shipment to storage	0	0	1×10^5	2	4×10^5	7

Source: U.S. Atomic Energy Commission 1972.

(Gillette 1973), where 4 curies of plutonium and 54,000 curies of ^{137}Cs and ^{90}Sr were released.

In addition and possibly of equal significance, as the quantity of transuranic materials increases, the possibility of diversion to unauthorized and assumably dispersive uses poses an increasing threat.

Ocean Dumping

Significant quantities of transuranics have been discharged to the deep ocean by containerized disposal operations conducted under the auspices of the Nuclear Energy Agency (NEA) of the Organization for Economic Cooperation and Development (OECD). These operations commenced in 1967 and have been carried out in the Northeast Atlantic Ocean (Table 3-8). Procedurally, the wastes are usually imbedded in a bitumen or concrete matrix inside a 220-liter steel drum and dumped at depths of approximately 5,000 meters.

TABLE 3-8

Ocean Dumping of Transuranic Elements in the Northeast Atlantic

Year	Estimated Total Alpha Activity (Ci)
1967	253
1969	500
1971	630
1972	681
1973	740

Source: Olivier 1974, pers. comm.

A hazard evaluation model and assessment of limits for these disposal operations have been developed by Webb and Morley (1973). Currently, the International Atomic Energy Agency, pursuant to its responsibilities under the International Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, is developing guidelines regarding ocean disposal of radioactive wastes which include specific reference to transuranics.

The projected growth of the nuclear power-generating industry may result in increasing pressure to dispose of not only fuel reprocessing and fabrication wastes, but also used reactor vessels into the oceans. Present United States policy, as reflected in Public Law 92-523 (Marine Protection, Research, and Sanctuaries Act of 1972), prohibits the ocean disposal of radiological warfare agents and high-level radioactive waste. In addition, regulations and criteria developed to implement this law require placing all other radioactive material in containers and a site-specific environmental effects evaluation prior to any permit consideration. Currently there are no proposals in the U.S. for ocean dumping of radioactive wastes.

Effluent Waste Disposal

As a consequence of the operation of the one-pass coolant reactors at the Hanford facility, considerable amounts of ^{239}Np, generated by neutron-capture on the natural ^{238}U in the river water coolant, were released into the Columbia River (Foster and Soldat 1966, Foster 1973). With the advent of closed-loop cooling and the recent shutdown of the last of the production reactors, transuranic releases to the coastal waters have stopped.

Since 1957 the United Kingdom has released, by pipeline into the Irish Sea off Windscale, low-level, aged, liquid wastes from their fuel reprocessing plant (Joseph *et al.* 1971). The part consisting of alpha radioactivity (largely transuranic nuclides) has progressively increased by 20 to 100 percent per year for every year of operation through 1969. This was the only increasing category of discharged artificial radioactivity. By 1970, the annual release had reached 1500 curies total alpha, or 84 percent of the authorized amount. In November 1970, the authorized amount was increased from 1800 curies to 6000 curies total alpha per year (Mitchell 1971a, b).

The three other British activities that involve release of alpha radioactivity in their wastes--Winfrith, Springfields, and Dounreay--are reported to have been relatively insignificant in amounts released in 1970; less than 12, 18, and 120 curies, respectively (Mitchell 1971b). These sites have authorized release rates of alpha emitters of 1200, 360, and 240 curies per year, respectively.

It has been argued (Jeffries *et al.* 1973), on the basis of monitoring data accumulated by Mitchell (1970, 1971a, b) and by the Bundesminister für Bildung und Wissenschaft (1972), that liquid waste from the French fuel reprocessing plant at Cap de la Hague is most probably responsible for an injection of ^{137}Cs into the southwestern North Sea. It seems to us most unlikely that a ^{137}Cs rich effluent from such an activity would be free of transuranics, but no monitoring data or waste stream data are available. Joseph *et al.* (1971) stated that this plant indeed intended to dispose of treated wastes directly into the English Channel (Avargues and Jammet 1966).

The recently completed and operating Italian fuel reprocessing plant, La Trisaia, on the Gulf of Taranto, is designed to release treated waste effluents to the near shore marine environment (Marzocchi *et al.* 1971). At this time, no information is available regarding the amounts or the planned limits of transuranic discharge, but data presented by Schreiber *et al.* (1971) suggest that transuranics will be present. The Indian fuel reprocessing plant at Trombay discharges low-level liquid wastes to the bay there, as will the new large reprocessing plant being built at Tarapur (Pillai and Kamath 1971); no data have yet been published showing the transuranic content of these discharges. In this case, however, a monitoring operation capable of surveying the transuranic problems is set up in Bombay (Pillai 1973, pers. comm.).

The decisions which appear to have been made in France, Italy, India, and Great Britain to discharge liquid low-level reprocessing wastes directly to the coastal ocean are suggestive of future increasing pressures for more ocean disposal.

Other Sources

^{238}Pu is now used as fuel in electrical and heat generating units, and this use is expected to increase with time. ^{238}Pu was chosen for these applications because of its half-life, (87.8 years) intermediate decay energy, high power density, and comparatively low cost.

The primary use of these radioisotope thermogenerators (RTG) in the U.S. has been in the space program providing power to various unmanned satellites and for several of the experiments on the surface of the moon. Three aborted space experiments resulted in return of the RTG's to the earth's surface. In 1964, SNAP-9A disintegrated upon re-entry into the atmosphere (Hardy *et al.* 1973). The fine particles of released ^{238}Pu behaved very much like fallout from nuclear weapons tests and ultimately deposited about 1.1 x 10^4 Ci of ^{238}Pu in the world ocean. A second incident occurred in 1968 when a satellite bearing a SNAP-19 generator containing about 4 x 10^4 Ci of ^{238}Pu failed to achieve orbit. The device was retrieved intact from shallow water off the coast of California. About the same quantity of ^{238}Pu returned to earth with the aborted Apollo 13 spacecraft, in 1970. This unit, the SNAP-27, was deposited intact in the deep Pacific Ocean, near the Philippine Trench. It should be noted that, upon re-entry, each of the three units described above performed as it had been designed to perform.

Another use of transuranics in the not too distant future will be in the medical field. The present emphasis is on the electrical heart pacemaker utilizing ^{238}Pu. The units presently designed use about 8 Ci and have a working life of about 10 years (Crandall 1971). Projections are available to indicate that on the order of 10^6 individuals in the U.S. will have nuclear pacemakers by 2000, and hence in excess of 10^6 Ci of ^{238}Pu will be involved (Crandall 1971, Mott *et al.* 1972, Seaborg 1973). A second medical application is proposed artificial heart pump, utilizing about 1000 Ci of the nuclide (Mott *et al.* 1972).

ENVIRONMENTAL BEHAVIOR

Non-Marine

Numerous articles describing the behavior of the transuranics in the nonmarine environment have been published (Krey *et al.* 1962, Olafson and Larson 1963, Magno *et al.* 1967, Romney *et al.* 1970, Langham 1971, Krey and Krajewski 1972, Volchok *et al.* 1972, Price 1973). In many of the analyses of atmospheric samples, the ratio $^{239}Pu/^{90}Sr$ is relatively constant (range .012 to .046, average .030, and 100 percent relative standard deviation). Through knowledge of the temporal and latitudinal distribution of ^{90}Sr fallout delivery to the continents, estimates of ^{239}Pu deliveries to the oceans can be made (Noshkin and Bowen 1973). A similar case can be made for ^{241}Am. For ^{238}Pu, the extrapolation is slightly complicated by additional input from the SNAP-9A accident mentioned earlier.

The solubility of ^{241}Am is higher than ^{238}Pu and ^{239}Pu in various media (Price 1973, Raabe *et al.* 1973). Within a limited geographical area of Pu contamination, the ratio $^{239}Pu/^{238}Pu$ varied from 20 in the surface soil, to 10 in the vegetation, to 1 in rodents in the vicinity (Hakonson and Johnson 1973). In soil, the ratio $^{239}Pu/^{241}Am$ decreased with depth, again probably reflecting the greater solubility of ^{241}Am.

Marine

Transuranic elements have been introduced to the environment in dispersed form in three ways:

1. Local and worldwide fallout from nuclear explosives testing;
2. Atmospheric burn-up of plutonium power supplies and nuclear weapons (e.g. Thule, Greenland); and
3. Fluid wastes from chemical reprocessing and reactor operations.

The environmental redistributions of plutonium, after its introduction by each of these avenues, have been studied to some extent, and a small amount of information about americium is available. For the other elements listed in

Table 3-2, we have either isolated data points, or no information. It is important to emphasize that these three avenues of introduction are qualitatively different. Materials from the first are more or less mixed in fused particles with other constituents of the device and of its environment, although the range of particle sizes varies. The second source should provide a mixture of oxide particles of higher purity than the first. The third source can be assumed to introduce the elements in soluble forms so that their movement is controlled to some extent by their aquatic chemistry. In general, the range of elements and of nuclides represented is much greater for the third source. Unfortunately, the data now at hand do not permit us to distinguish among the distributions of plutonium, following its introduction in different ways. It has been assumed by Bowen and his co-workers (Wong *et al.* 1970a, b, Bowen *et al.* 1971, Noshkin and Bowen 1973) that both plutonium and americium from worldwide fallout pass through soluble phases in the oceans, but this has not yet been confirmed.

In the oceans, Pillai *et al.* (1964) found that plutonium concentrations in surface water samples collected while fallout rates were high were explainable by considering the precipitation exposure of the water masses sampled. More recently, samples collected while fallout rates were low showed lower concentrations that were explained by sedimentation of plutonium. This was in contrast to the conservative behavior of ^{90}Sr and ^{137}Cs in the same samples (Miyake and Sugimura 1968, Miyake *et al.* 1970, Bowen *et al.* 1971, Noshkin 1972, Noshkin and Bowen 1973). Noshkin and Bowen (1973) studied the relationship between the ^{239}Pu in the sediment (expressed as a fraction of the estimated delivery to the latitude sampled) and the depth of the overlying water. Several shallow water cores contained 100 percent of the predicted delivery, whereas their deepest core (over 5300 m) contained no measurable ^{239}Pu. All their Atlantic data could be explained by assuming ^{239}Pu was removed in association with a population of particles of various sinking rates (30 percent at 392 m/yr; 40 percent at 140 m/yr; 30 percent at 70 m/yr). This curve also predicted very well the mean fractions of delivery found at various depths in several Atlantic Ocean water columns, although each water column was unique in some details. These findings led them to believe that the major marine removal pathway for this transuranic was in sedimenting biogenous particles. This was supported by the fact that the biologically unproductive Mediterranean gave data that were displaced systematically in the direction of less ^{239}Pu removal to the sediments.

We found that present data are insufficient to show that this behavior can be generalized for other transuranic elements, or even for the ^{238}Pu that was introduced by SNAP-9A. Sugihara and Bowen (1962) and Bowen and Sugihara (1965) concluded that lanthanide sorption was usually on inorganic particulates and americium is much more lanthanide-like than plutonium. Unpublished data show, in one North Atlantic water column, a steady increase with depth of the $^{241}Am/^{239}Pu$ ratio, from 0.16 at 200 m to 0.38 at 3200 m (Bowen 1973, pers. comm.). This appears to us to be too great an increase to be explained by generation of ^{241}Am by decay of ^{241}Pu, and in that case, would argue strongly for control of plutonium and americium distributions by their solution chemistry in seawater.

Aarkrog's (1971) study of the accidental burn-up release of ^{239}Pu and ^{241}Am near Thule, Greenland, showed that 99 percent of the Pu measured went to the sediments; the 1 percent staying in the water column was largely particulate (as was to be expected of newly formed PuO_2 particles). The reprocessing waste discharge into the Irish Sea from Windscale also results (Preston and Mitchell 1973, Mitchell 1971a,b) in association of most of the ^{239}Pu and ^{241}Am with the sediments close to the discharge area. In our estimation, the biological data are not yet sufficient to show the extent of chemical remobilization of the ^{239}Pu, and we found no studies of ^{241}Am.

Studies of marine and freshwater sediment columns indicate, as do those of soil columns, unexpected vertical mobility of ^{239}Pu and ^{241}Am (Noshkin and Bowen 1973, Bojanowski *et al.* in press). It is the impression of some that this mobility is too great to be explained just by biological reworking. It is well known that soil solution and sediment interstitial waters contain complexing agents that could solubilize Pu, Am, or other transuranics. Orthophosphate is the most generally abundant solubilizer, although not the most effective.

Several lines of argument lead to the conclusion that sediment ^{239}Pu is remobilized in a form more available to organisms. Adams and Fowler (1970) found that there was a gradual increase, with time, of plutonium in the gut of fish which lived in a plutonium-contaminated aquarium.

Bottom feeding fish tend to show higher liver ^{239}Pu than those feeding higher in the water column; and a similar, although less strong, tendency is shown by sediment-ingesting invertebrates (Noshkin 1972).

We are almost ignorant of the biological or environmental significance of the behavior of transuranic elements once they are incorporated into marine sediments.

^{239}Pu and ^{241}Am from fallout have been found whenever sought in marine organisms from a variety of places in both hemispheres (Noshkin 1972, Cherry and Shannon, in press). ^{242}Cm has been found in Fucus from the Irish Sea (Livingston 1973, pers. comm.), and ^{237}Np (at very low levels) in a variety of samples from Eniwetok (Noshkin 1973, pers. comm.). However, data are not sufficient to allow interpretations of environmental behavior.

Polykarpov (1966) reports on studies which indicate concentration factors of about 1000 for ^{239}Pu in marine plants; Noshkin (1973) has tabulated more recent data (Table 3-9) showing that this level is often exceeded by marine benthos and plankton and is usually exceeded by the Atlantic Ocean species of pelagic *Sargassum*.

Data reported by Bojanowski *et al.* (in press) and by Mitchell (1971a,b) show that ^{241}Am from fallout or from waste is strongly concentrated by *Sargassum* or rooted algae leading to in-plant ratios of ^{241}Am/^{239}Pu several times higher than those found in the medium. Their data indicate that ^{241}Am is more concentrated in Porphyra from the Irish Sea (as ^{144}Ce had been shown to be) when contrasted with *Fucus* (^{241}Am/^{239}Pu as high as 1.4 in Porphyra versus 0.18 in Fucus). This would have been expected by the analogy between americium and cesium.

A study by Wong *et al.* (1972) showed that in the great Pacific kelp, *Pelagophycus porra*, inner parts contained ^{239}Pu concentrations approximately 1/200 of that in the thin outer layers of the plant. Noshkin (1972) and Wong *et al.* (1972) suggest that this shows redistribution of the plutonium, after adsorption uptake, by the plant's active metabolism.

Zlobin has studied the mechanisms of accumulation of ^{239}Pu in marine algae, especially in the brown alga (*Ascophyllum nodosum*) (Zlobin 1966, 1971, Zlobin and Mokanu

TABLE 3-9

Plutonium in Marine Organisms

Organism	Collection Date	Location	Tissue and Number of Samples	Mean ^{239}Pu pCi/kg wet	$\frac{^{238}Pu}{^{239}Pu}$	Range of Concentration Factors
Plants						
Algae (attached)	1964	California Coast	Whole (4)	0.47	--	660-1570
	1970-1971	Cape Cod, Mass.	" (6)	0.53	--	100-1600
	1971	California Coast	" (19)	0.64	--	260-3500
Sargassum (attached)	1971	California Coast	" (2)	0.28	--	325-450
Sargassum (pelagic)	1965-1971	Atlantic Ocean	" (6)	20.7	--	3,000-100,000
Animals						
Plankton (mixed)	1950	California Coast	" (1)	0.023	--	--
	1961	Atlantic Ocean	" (1)	2.03	--	2,300
	1964	California Coast	" (1)	1.08	--	2,600
Sponge	1970	Cape Cod, Mass.	" (1)	1.80	0.07	2,100
Annelid Worm	1970	Cape Cod, Mass.	" (1)	3.50	0.06	4,100
Starfish	1970	Cape Cod, Mass.	" (1)	0.87	0.09	1,020

(continued)

TABLE 3-9 (continued)

Gastropods	1970	Cape Cod, Mass.	Body (2)	0.35	0.05	140-660
	1970	Cape Cod, Mass.	Shell (2)	0.42	0.09	300-690
Bivalves	1964	California Coast	Body (2)	0.22	--	230-290
	1968	Danish Coast	? (1)	7	--	8,200
	1970	Cape Cod, Mass.	Body (5)	0.31	0.07	300-520
	1970	Cape Cod, Mass.	Shell (2)	0.47	0.08	490-600
Salpa	1958	Atlantic Ocean	Whole (3)	1.40	--	900-2400
Crustacea	1968	Danish Coast	Whole (5)	1.5	--	1,060-4,500
Fish	1964	California Coast	Whole (1)	0.001	--	3
	1969	Cape Cod, Mass.	Muscle(1)	0.005	--	1-5
	1969	Cape Cod, Mass.	Liver (1)	0.03	--	---
	1969	Cape Cod, Mass.	Bone (1)	0.6	--	---
	1970	Cape Cod, Mass.	Muscle(3)	0.003	--	1-2
	1970	Cape Cod, Mass.	Liver (3)	0.05	--	14-60
	1970	Cape Cod, Mass.	Gut (3)	0.68	--	40-1100
	1970	Cape Cod, Mass.	Bone (3)	0.11	--	50-600
	1970	Cape Hatteras	Muscle(3)	0.003	--	4
	1970	Cape Hatteras	Liver (3)	0.15	--	175
	1970	Cape Hatteras	Bone (3)	0.02	--	21
	1971	Cape Hatteras	Muscle(2)	0.006	--	10-15
	1971	Cape Hatteras	Bone (2)	0.03	--	30-50

Source: Noshkin 1972.

1970, Zlobin and Perlyuk 1971). There appears to be a definite connection between ^{239}Pu assimilation and both photosynthesis and cyanide-poisonable respiration. An important question also raised by these studies is that of availability of a plant's physiologically-accumulated plutonium or americium to grazers. We know of no relevant data to resolve this question.

In general, it appears that marine invertebrates exhibit higher concentrations of fallout ^{239}Pu than the fish which were analyzed (Noshkin 1972). This is also the trend of the data on local fallout ^{239}Pu at the Pacific test sites. In fish, ^{239}Pu shows bone or liver-seeking behavior, as it does in mammals. Liver-seeking may also be characteristic of ^{239}Pu in mollusks and crustacea, but there are few data for these organisms. The high concentrations of ^{239}Pu associated with shells of mollusks and lobsters can be explained by the tendency for shell-periphyton to accumulate trace constituents from the medium, rather than by the invertebrate equivalent of bone-seeking.

Patin *et al.* (1971) studied the accumulation of ^{239}Pu by spawn of the fish *Misgurnus fossilis*. Although ^{239}Pu uptake was less efficient than has been described for ^{90}Y, the kinetics of the two are quite similar. It appears that there are critical stages in embryogeny when the membranes are much more effective at ^{239}Pu uptake than they are at other times. This and the fact that EDTA complexation seemed to have no effect on the shape of the uptake curve suggest that aquatic embryos may present special problems in respect to transuranic uptake, and hence to the study of toxicity.

The data show little evidence for any trophic level enhancement of ^{239}Pu accumulation although, in the one case specifically studied, starfish showed consistently higher ^{239}Pu from fallout than did the mussels on which they were feeding (Wong *et al.* 1970 b).

By analogy, we would expect ^{239}Pu or ^{241}Am, once incorporated in tissues of marine organisms, to show long residence times; in the case studied, Hodge *et al.* (1973) suggested a residence half-time of 3.5 years for ^{239}Pu in albacore liver.

The radiobiology of aquatic organisms has been less adequately studied than that of their terrestrial counterparts. Nevertheless, a significant literature exists, particularly with regard to effects of importance to commercial fisheries. In general, the radiosensitivity of aquatic organisms does not appear to be markedly different from that of nonaquatic organisms although it is frequently assumed that adult aquatic forms are more resistant. In both terrestrial and aquatic forms, the developmental stages are by far the most sensitive.

However, there are large gaps in our knowledge. Only a relatively few organisms have been studied in relation to the number and variety of marine species. Large concentration factors of radionuclides have been documented for certain organisms and these indicate much larger doses to the concentrating organism than the concentration of the nuclide in seawater would predict. These factors are known less well for the transuranic nuclides than for many other radionuclides. The interaction of radiation effects with other environmental factors is also only beginning to be studied.

It has been argued (Mitchell 1971a,b) that plutonium and americium from reprocessing wastes represent, even at the Windscale levels of release, negligible radiobiological hazards. This argument has been used as the basis for a sharp increase in Windscale's authorized annual release of alpha activity commencing in November, 1970. The basis for this position is the explicit assumption that ^{239}Pu or ^{241}Am in laver bread (foodstuff made from Porphyra) will pass through the gut wall with the same low efficiency reported for ^{239}Pu added to the diets of experimental rats and mice. We submit that this assumption should be tested. Coupled with the argument is the statement that no other pathway to man is known. An obvious counter to this is the frequency with which potato fields in some coastal areas are fertilized with *Fucus* and other rooted algae. All too few analyses are available of mussels, clams, oysters, and the other marine bivalves that so often concentrate trace constituents of their environments, and no data, support the assumption of the dietary unavailability of the transuranics so accumulated.

OVERVIEW

On balance, our findings indicate an insufficiency of information regarding the chemical and biological behavior of the transuranics in the marine environment. Without such information meaningful quantitative assessment of either current or future impacts is not possible. We cannot dismiss the possibility that marine concentrations of one or more transuranics may approach levels of concern through naturally-acting mechanisms which we do not understand. Present evidence indicates that transuranic elements introduced to marine waters are rapidly transferred to the sediments. If this holds true, then any input from waste treatment or reprocessing will mainly affect the coastal zone near the point of introduction. These sources would, then, not be expected to contribute significantly to open ocean pollution which would be largely due to fallout from atmospheric releases. Predictions of the effects of transuranic elements on the marine environment cannot be formulated until more extensive knowledge of their modes of transport and their biogeochemical and radiobiological behavior is available. On this basis, we recommend conservative approaches to any releases of transuranic elements to the environment. This applies to planning against accidental releases as well as to any planned releases. Both should be kept to an absolute minimum. Recommendations are detailed in Chapter 1.

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CHAPTER 4

SYNTHETIC ORGANIC CHEMICALS

Workshop Panel

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Background Paper

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In the past few decades, an expanding chemical industry has developed countless new organic chemical products and has increased product applications. Consumer acceptance and demand for more plastics, copolymers, synthetic fibers, and artificial rubbers has contributed substantially to the increasing output of major petrochemical facilities. Halogenated forms of the basic fossil-fuel-derived hydrocarbons have gained wide acceptance as pesticides, solvents, heat exchangers, dielectrics, and polymer intermediates because of their relative chemical stability. The overall volume of synthetic organic chemicals produced will continue to expand as the diversity of uses of these chemical products increases. Organisms encountering these synthetic molecules may be confronted with new metabolic problems in uptake, assimilation, detoxification, and elimination.

The marine environment is the ultimate reservoir for many waterborne and windborne substances. Unfortunately, the misconception that the oceans represent an unlimited sink for man-generated compounds still prevails. Mixtures of organic chemicals, including aromatic and chlorinated hydrocarbons, flow into coastal rivers and estuaries. Toxic wastes containing numerous biocidal chemicals are dumped at sea. The fate of this synthetic organic chemical input and its effect on the biological resources of the ocean is currently unknown and should remain a high priority item for marine research.

This chapter seeks to provide a pattern for the identification of synthetic organic compounds whose effects are not yet obvious, but which may represent a threat to marine ecosystems. The general criteria for selection of the substances examined were: (1) annual production; (2) patterns of use and dispersal; (3) toxicity; (4) bioaccumulation; and (5) persistence, as discussed in Chapter 2.

The substances which we evaluated were: perchloroethylene, 1,1,1-trichloroethane; propylene dichloride, ethylene dichloride, bis(chloroethyl)ether, benzene, toluene, acrylonitrile, hexachlorobenzene, and benzidene. We found insufficient information on bis(chloroethyl)ether and benzidene. Hence, we were not able to evaluate their potential for becoming ocean pollutants and they are not included in this report.

LOW MOLECULAR WEIGHT CHLORINATED HYDROCARBONS

Introduction

Chlorinated hydrocarbons occupy an important position in industrial society. Their development began in the first part of this century. In the 1920's and 1930's their production was accelerated by the emergence of liquid chlorine as a major commercial commodity. Following World War II, the chlorinated hydrocarbons rose to a dominant position in the chemical industry paralleling the growth of the entire organic chemical industry and the expansion of the petroleum industry. In 1948, 7.7 x 10^5 tons* of chlorinated hydrocarbons were produced in the United States; by 1970 production had risen to 8.2 x 10^6 tons. The U.S. production of ethylene dichloride alone was 4 x 10^6 tons in 1972 (ranking 13th in U.S. chemical production).

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*All units used in the report are metric unless otherwise indicated.

There is a wide variety of uses for chlorinated hydrocarbons including aerosol propellants, fumigants, fire extinguishers, flame retardants, hydraulic fluids, refrigerants, solvents, heat transfer agents, dielectric insulators, and intermediates in organic synthesis. Zitko and Choi (1971) listed over 120 halogenated paraffins, olefins, and aromatics industrially produced for one or more of these uses. The 1971 U.S. Tariff Commission Report on Production and Sales of chlorinated hydrocarbons in the United States (Table 4-1) shows that the majority of the chlorinated products consists of the low molecular weight halogenated hydrocarbons (C_1 to C_3).

The low molecular weight chlorinated compounds differ from the chlorinated aromatic hydrocarbons, such as DDT, PCB, and dieldrin, in several important ways. They have a much higher vapor pressure and thus tend to partition into the atmosphere. Their bioaccumulation factors are 100 to 1000 times smaller, and their water solubility, although low, is considerably higher. Their dispersive uses result primarily in release to the atmosphere. Many of them undergo more rapid photolysis in the atmosphere, hydrolysis in water, and biological degradation in water and soils than their heavier aromatic counterparts.

This section will deal with four representative low molecular weight chlorinated hydrocarbons: tetrachloroethylene (Per); 1,1,1-trichloroethane (1,1,1-TCE); 1,2-dichloroethane (EDC); and 1,2-dichloropropane (PDC). Per and 1,1,1-TCE are used in dry cleaning and degreasing and have primarily dispersive uses. The major uses of EDC and PDC are as chemical intermediates and they thus have largely not been introduced to the environment as a direct result of their uses. The term "low molecular weight chlorinated hydrocarbons" here refers to C_2 to C_3 chlorinated hydrocarbons, and is abbreviated LMCH.

TABLE 4-1

U.S. Production and Sales of Halogenated Hydrocarbons in 1971

Halogenated Hydrocarbons	Production (Metric Tons x 10^3)	Sales (Metric Tons x 10^3)
Total	8,560	3,960
Carbon tetrachloride	493	361
Chlorinated paraffins, total	26.1	27.2
35-64% chlorine	19.8	20.8
Other	6.4	6.4
1-Chlorobutane (n-butyl chloride)	1.8	1.8
Chlorodiflurormethane	--	1.8
1-Chloro-1,1-difluoroethane	--	0.1
Chloroethane (Ethyl chloride)	281	110
Chloroform	104	62.9
Chloromethane (Methyl chloride)	198	87.5
1,2-Dibromoethane (Ethylene dibromide)	127	78.7
Dichlorodifluoromethane	176	169
1,2-Dichloroethane	3,423	594
Dichloromethane (Methylene chloride)	182	166
1,2-Dichloropropane (PPC)	--	11.1
Iodomethane (Methyl iodide)	--	.01
Tetrachloroethylene	319	296
1,1,1-Trichloroethane (Methyl-chloroform)	169	154
Trichloroethylene (TCE)	232	241
Trichlorofluoromethane	117	107
Vinyl chloride, monomer (Chloroethylene)	1,963	1,360
All other halogenated hydrocarbons	779	70.6

Source: U.S. Tariff Commission 1973.

Physical Properties, Production, and Consumption

Tetrachloroethylene (Per)

Physical Properties Per (1,1,2,2-tetrachloroethylene or perchloroethylene) is a clear, colorless, heavy, non-flammable liquid with a distinctive ethereal odor. It has the chemical formula $CCl_2=CCl_2$ and a molecular weight of 165.85. It is known commonly in the chemical industry as Per and is sold under a number of trade names including Dee-Solv, Dow-Per, Percosolv, Perclene, Nema, Per Sec, Tetracap, and Tetropil. It is a powerful solvent for a large number of organic substances including alcohols, ethers, oils, fats, tars, rubber, resins, and acids such as benzoic, cinnamic phenylacetic and salicyclic. It is miscible with other chlorinated organic solvents and with many other common organic solvents. Per does not dissolve sugars, glycerol, proteins, or casein. It has a water solubility of 150 ppm by weight, and water has a solubility of 8 ppm in Per (Hardie 1964). The following are some of Per's physical properties:

Boiling point:	121 C @ 760 mm Hg
Freezing point:	-22.7 C
Specific gravity:	1.62260 @ 20 C
Vapor density:	5.8 (air = 1.0)
Viscosity, liquid:	0.839 cP @ 25 C
Flash point:	None
Specific heat:	Liquid: 0.205 cal/g-C° @ 20 C Vapor: 0.146 cal/g-C° @ 100 C, 1 atm.
Latent heat of vaporization:	8.3 kcal/g-mole
Latent heat of fusion:	2.525 kcal/g-mole
Refractive index:	1.5029 @ 25 C

Vapor pressure:

C°	mm Hg	C°	mm Hg
-20.6	1	70	155.3
+ 2.4	5	80	226.0
13.8	10	90	319.2
26.3	20	100	438.5
40.0	41	110	591.6
50.0	67	121	760.0

Dipole moment: zero

Production The first industrial production of Per began in Germany and the United Kingdom shortly before the First World War, and in the United States in 1925. Production ceased during World War I. In the 1920's and 1930's development of small drycleaning units stimulated the demand for Per in the United States, while in the United Kingdom and Europe trichloroethylene continued to be the principal drycleaning solvent. Following World War II, Per displaced carbon tetrachloride as the dominant drycleaning fluid in the United States and continued to make inroads into the use of trichloroethylene in Europe and the United Kingdom (Hardie 1964). In the 1930's Australia and New Zealand were importing a significant tonnage to combat the liver fluke in sheep.

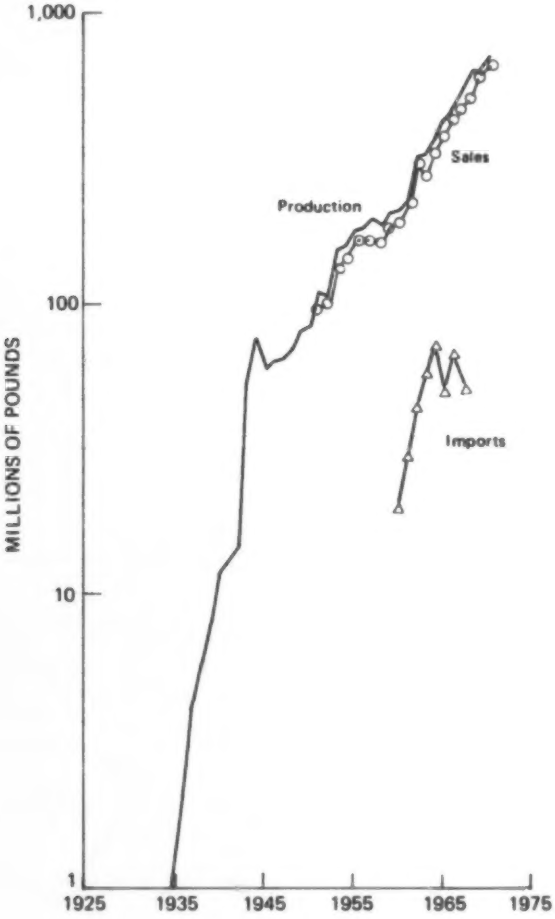
Per is produced in the United States by nine companies (U.S. Tariff Commission 1973) in fourteen locations (Stanford Research Institute 1968, U.S. EPA OHM-TAD, unpub. data) (Table 4-2). Production has grown steadily over the last 45 years at an annual rate of 9 percent (Figure 4-1), reaching 3.33×10^5 tons in 1972. The Chemical Economics Handbook (Stanford Research Institute 1972) estimates Per production will increase at an annual rate of 5 to 7 percent over the next few years. The largest production capacity is centered along the lower Mississippi River and the upper Texas Gulf Coast (Table 4.2).

TABLE 4-2

U.S. Tetrachloroethylene (Per)
Producing Companies, Plant Locations and Capacities
(June 1, 1968)

Company and Location	Annual Capacity (Metric Tons)	Raw Materials
Diamond Shamrock Chemical Co.		
Deer Park, Texas	45,000	EDC
The Dow Chemical Co.		
Freeport, Texas Pittsburg, California Plaquemine, Louisiana	108,000	Various
E.I. duPont de Nemours & Co.		
Niagara Falls, New York	27,000	Acetylene
Vulcan Materials Co.		
Geismar, Louisiana	27,000	EDC
Wichita, Kansas	13,000	EDC
Hooker Chemical Corp.		
Tacoma, Washington	4,500	Acetylene
Taft, Louisiana	16,000	Acetylene
PPG Industries, Inc.		
Barberton, Ohio	9,000	Ethane & propane
Lake Charles, Louisiana	23,000	EDC
Stauffer Chemical Co.		
Louisville, Kentucky	32,000	Various
Ethyl Corporation		
Baton Rouge, Louisiana	23,000	EDC
Detrex Chemical Industries, Inc.		
Ashtabula, Ohio	11,000	Acetylene

Source: Stanford Research Institute 1968



Sources: U.S. Tariff Commission, 1970 and 1971.
Stanford Research Institute, August, 1968.
Anonymous (Chemical Week) May 2, 1953.
Anonymous (Chemical and Engineering News) 1973.

FIGURE 4-1

U.S. Production, Sales, and Imports of Tetrachloroethylene

U.S. exports of Per, mostly to western Europe, accounted for approximately 15 percent (5×10^3 tons) of the U.S. production in 1972. Imports have shown a steady decline for several years and were $1\text{-}2 \times 10^4$ tons for 1972.

There are no reported figures for total world production of Per. The Chemical Economics Handbook (Stanford Research Institute 1968) lists 25 foreign companies primarily in industrial countries producing Per. If we assume that the United States production is roughly one-third of the world production, based on approximations of Gross National Product (U.S. x 3 = World), the total world production of Per would be approximately 10^6 tons per year.

Manufacturing Process The classical production method of Per is closely associated with the production of trichloroethylene. It consists of a four-step conversion of acetylene involving successive chlorinations and dehydrochlorinations. In 1966, 20 percent of Per was produced in this manner (Stanford Research Institute 1968).

Today most Per is produced from oxyhydrochlorination, chlorination, or dehydrochlorination of other chlorinated hydrocarbons using the following raw materials (Stanford Research Institute 1968, Miller 1966):

1. Ethylene and EDC.
2. Methane, ethane, propane, butane and iso-butane.
3. Propylene and PDC (the latter is obtained as a by-product of propylene-oxide manufacture).
4. Various chlorinated materials, such as 1,1,2-trichloroethane, that are the "bottoms" obtained in cracking EDC for vinyl chloride manufacture.

Other chlorinated compounds are usually produced with Per, the quantities and types dependent upon the reaction conditions. Small quantities of stabilizers are added to the commercial product to inhibit decomposition.

Consumption The major uses of Per are in dry cleaning, vapor degreasing, and as a chemical intermediate. The Chemical Economics Handbook (Stanford Research Institute 1972) estimates the following percentage usage of Per for 1969:

Use	Percent of Production	Tons/Year (1972)
Dry cleaning	65 - 70	222,000
Vapor degreasing	17	55,000
Chemical intermediates	11	36,000
Miscellaneous	2 - 7	19,000

Per is the dominant solvent currently used in the dry cleaning industry. It is an excellent fabric cleaner, is easily recycled, and is nonflammable.

Per had about 10 percent of the market for vapor degreasing in 1968 (Stanford Research Institute 1968). It is used in some applications because of its ability to dry water wet metals and to dissolve waxes.

Per is also used in the synthesis of fluorocarbons and as an intermediate for production of trichloroacetic acid. Other uses are as a solvent for silicones, a carrier for fabric finished, and a vermifuge. It has been used medically to control hookworm, tapeworm, pinworm, whipworm, and liver fluke. Its veterinary use is for hookworms in many animal species, ascarids of dogs and cats, and stomach worms in cattle, sheep and rabbits.

1,1,1-Trichloroethane (1,1,1-TCE)

Physical Properties Trichloroethane (1,1,1-trichloroethane or methyl chloroform) is a clear, colorless, heavy, nonflammable liquid with a characteristic odor. Its chemical formula is CCl_3CH_3 and its molecular weight is 133.42. It is commonly known in the chemical industry as 1,1,1-TCE and sold under a number of trade names including Chlorothene, Triethane, and Genklene. It is a solvent for fats, greases, waxes, resins, oils, and a wide range of organic materials and compounds. It is miscible with alcohols, ethers, esters, ketones, benzene, the chlorinated hydrocarbons and with other common organic solvents. It has a water solubility at 20 C of 4400 ppm (by weight), and water has a solubility of 500 ppm in 1,1,1-TCE (Hardie 1964). The following are some of its physical properties:

Boiling point:	74.0 C @ 760 mm Hg
Melting point:	-32.62 C
Specific gravity:	1.34587 @ 15 C
Vapor density:	4.6 g/liter, 760 mm Hg, bp
Viscosity, liquid:	0.093 cP @ 15 C
Surface tension:	25.56 dyn/cm @ 20 C
Flash point:	None
Specific heat, liquid:	0.2552 cal/g-C av, -15 to 26 C
Refractive index:	1.4379 @ 20 C

Vapor pressure:

C°	mm Hg	C°	mm Hg
0	37	50	340
10	62	60	470
20	100	70	660
30	150	80	900
40	240		

Production Commercial production of 1,1,1-TCE began in 1951 under the trademark Chlorothene (Dow Chemical, USA). Since that time, 1,1,1-TCE has increased in use in the cold cleaning field (ambient temperature solvent cleaning) and in several other solvent applications. The compound is in large-tonnage production in the United States, the United Kingdom (Hardie 1964), and continental Europe.

Table 4-3 shows the U.S. production and sale of 1,1,1-TCE over the last several years. Four companies in the United States (U.S. Tariff Commission 1971) and two in the United Kingdom (Chemical Industries Association, Ltd. 1970) produce the compound. The U.S. production sites are located on the upper Gulf of Mexico coast (Table 4-4).

TABLE 4-3

United States Production and Sales of 1,1,1-Trichloroethane

Year	Number of Manufacturers	Production (Metric Tons)	Sales Quantity (Metric Tons)
1971	4	169,000	154,000
1970	4	166,000	148,000
1969	3	147,000	135,000
1968	3	136,000	130,000
1967	3	-	122,000
1966	4	110,000	113,000
1965		-	-
1964		-	-
1963		-	-
1962		18,000	-
1961		9,000	-

Source: U.S. Tariff Commission 1968-1973, Hardie 1964

TABLE 4-4

United States Producers of 1,1,1-Trichloroethane and Production Sites

Company[1]	Production Site[2]
The Dow Chemical Company	Freeport, Texas
Vulcan Material Company	Geismar, Louisiana
Pittsburg Plate Glass Company	Lake Charles, Louisiana
Ethyl Corporation	Baton Rouge, Louisiana

[1] Company list comes from 1972 U.S. Tariff Commission Reports and EPA's OHM-TAD SYSTEM, unpublished data.

[2] Production sites come from EPA's OHM-TAD SYSTEM, unpublished data.

Manufacturing Process 1,1,1-TCE, like many of the other chlorinated hydrocarbons, can be produced from several different starting materials and by several different methods. Starting materials include 1,1-dichloroethylene (U.S. Pat. 2,209,000, July 1940, Nutting and Huscher); 1,1-dichloroethane (Fr. Pat. 1,304,821, October 1961, Haefner and Sims); and 1,2-dichloroethane (U.S. Pat. 3,065,280, November 1962, H. J. Vogt).

1,1,1-TCE is usually sold with small amounts of stabilizing substances added to the commercial product. A number of different stabilizers have been patented but no definite information is available as to which are in current use.

Consumption The major use of 1,1,1-TCE is as a cold cleaning solvent. It can be used in almost any application where there is a need to remove greases, oils, tars and similar residues from surfaces at ambient temperatures. It is used in a wide range of industries including the aircraft industry for cleaning airframes, engine components, electronic instruments, and hydraulic systems; the electronics industry for cleaning such components as relays, resistors, and diodes; the printed circuit industry for selectively removing photoresistant inks, soldering flux, and other contaminants; the textile industry for cleaning yarns, threads, and finished cloth; and industries where there is a need to clean molds, castings, processing equipment, and other types of instruments and machinery. Some other uses of 1,1,1-TCE are as a solvent for germicides, insecticides in aerosols, and polystyrene in printing inks, and many contact adhesive applications. It is also used in the formulation of shoe polishes, lapping compounds, and clothing spot removers, as well as in the cleaning of fiber glass, business machines, and small electronic parts. In the grain industry, it is used in flotation of weevils and in the petroleum industry for the extraction of oil from well drilling cores. All of these uses can be classed as dispersive.

1,2-Dichloroethane (EDC)

Physical Properties 1,2-Dichloroethane (ethylene dichloride, ethylene chloride, s-dichloroethane) is a colorless liquid with an odor resembling that of chloroform. It has the chemical formula CH_2ClCH_2Cl and a molecular weight of 98.97. In the chemical industry, it is commonly known as EDC. The solubility of EDC at 20 C is 8690 ppm in water and the solubility of water in EDC at 20 C is 1690 ppm. It is miscible with all chlorinated organic solvents, alcohols, and ethers, and is a solvent for fats, greases, waxes, and many other organic compounds. Some of its physical properties are:

Boiling point:	83.5 C
Melting point:	-35.4 C
Specific gravity:	1.25280 @ 20 C
Vapor density:	1.26 g/liter, 760 mm Hg
Viscosity, liquid:	0.840 cP @ 20 C

Surface tension:	32.23 dyn/cm @ 20 C
Flash point:	21 C (open cup)
Specific heat:	liquid: 0.308 cal/g-C @ 20 C vapor: 0.255 cal/g-C @ 97.1 C, 1 atm.
Latent heat of vaporization:	77.3 cal/g, bp
Latent heat of fusion:	21.12 cal/g
Refractive index:	1.4449 @ 20 C
Dipole moment:	1.57×10^{-18} esu

Vapor pressure:

C°	mm Hg	C°	mm Hg
0	25	50	240
10	40	60	350
20	60	70	500
30	100	80	700
40	160	83.5	760

Production EDC was the earliest known chlorinated hydrocarbon, synthesized in 1795. EDC is produced in the United States by 12 companies at 16 production sites (Table 4-5). The major EDC producers are located along the lower Mississippi River and upper Texas coast of the Gulf of Mexico. Production has increased at an average annual rate of approximately 21 percent from 1963 to 1972 (Figure 4-2).

Exports of EDC were 1.7×10^5 tons in 1972 down from 3×10^5 metric tons in 1970. Imports were negligible (U.S. Bureau of the Census 1973).

The Chemical Economics Handbook (Stanford Research Institute January, 1972) lists 80 companies in 23 other countries producing EDC (Table 4-6) as of October 1971.

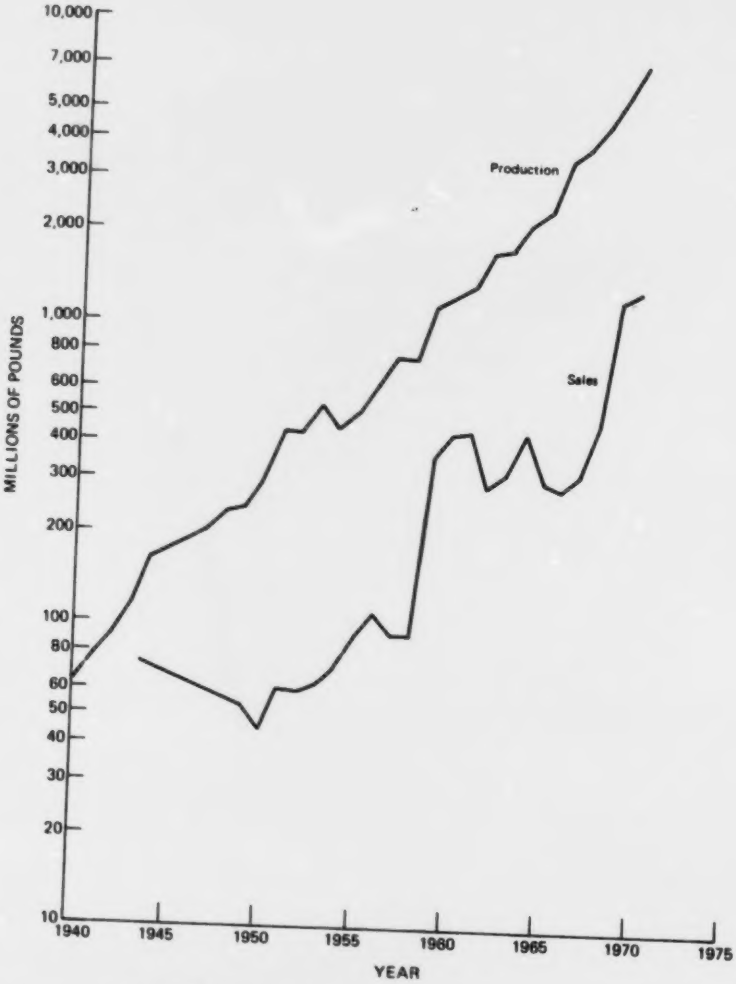
Manufacturing Process EDC is manufactured by the chlorination or oxychlorination of ethylene in the United States. The commercial product is usually stabilized by small amounts of alkylamines (about 0.1 percent by weight).

TABLE 4-5

U.S. Ethylene Dichloride Production

Company and Location	Annual Capacity as of October 1971 (Metric Tons)
Allied Chemical Corporation	
Baton Rouge, Louisiana	294,000
American Chemical Corporation	
Watson, California	147,000
Continental Oil Company	
Westlake, Louisiana	454,000
Diamond Shamrock Chemical Corporation	
Deer Park, Texas	118,000
The Dow Chemical Company	
Freeport Texas	498,000
Oyster Creek, Texas	453,000
Plaquemine, Louisiana	525,000
Ethyl Corporation	
Baton Rouge, Louisiana	249,000
Houston, Texas	118,000
The B. F. Goodrich Company	
Calvert City, Kentucky	408,000
Jefferson Chemical Company, Inc.	
Port Neches, Texas	31,000
PPG Industries, Inc.	
Lake Charles, Louisiana	453,000
Shell Oil Company	
Deer Park, Texas	543,000
Union Carbide Corporation	
Taft, Louisiana	68,000
Texas City, Texas	68,000
Vulcan Materials Company	
Geismar, Louisiana	108,000
Total Capacity as of October 1971	4,535,000

Source: Stanford Research Institute 1972



Source: U.S. Tariff Commission, 1962-1973

FIGURE 4-2

Production and Sales of Ethylene Dichloride

TABLE 4-6

Non-U.S. Ethylene Dichloride (EDC) Production Capacity

Area	Metric tons X 10^3 (As of October 1, 1971)	
North America		238
Canada	200	
Mexico	38	
South America		12
Peru	12	
Western Europe		3,885
Belgium	280	
France	650	
Germany	400	
Greece	50	
Italy	1,030	
The Netherlands	620	
Spain	45	
Sweden	140	
United Kingdom	670	
Eastern Europe		220
Rumania	40	
USSR	30	
Yugoslavia	150	
Asia		2,360
India	50	
Iran	35	
Japan	2,245	
Turkey	30	
Australia	100	100
Africa		120
Algeria	60	
South Africa	30	
UAR	30	
Total	6,935	
Future Total: January, 1973		9,600
January, 1974		10,800

Source: Stanford Research Institute January 1972

The largest percentage of EDC is produced by the chlorination of ethylene. This is carried out in either the liquid or gaseous phase using iron or other metallic chlorides as catalysts. Production yields from this process are 96 to 98 percent of the theoretical yield from ethylene (Stanford Research Institute 1972).

The production of EDC by the oxychlorination of ethylene is growing in importance. In this process ethylene reacts with air and hydrogen chloride in a fluid or fixed-bed process, and metallic chlorides are used as catalysts. Table 4-7 shows the composition of by-products from the oxychlorination of ethylene obtained from a petrochemical plant near Lake Charles, Louisiana (Jensen *et al.* 1970). These wastes are called "bottoms" or "EDC-tars". The exact composition of the EDC-tar is highly dependent on the manufacturing conditions and impurities in the ethylene feed.

Consumption The increased consumption of EDC from 1963 to 1972 largely reflected the increasing demand for vinyl chloride. Some of the other major uses of EDC include use as a lead scavenger in tetraethyl lead mixtures and as a starting material in the production of trichloroethylene, Per, methyl chloroform, ethyleneamines, and vinylidene chloride. Small amounts are used as solvents for various applications (e.g. textile cleaning and metal degreasing, and separation of wax from petroleum), as an intermediate in chemical synthesis (e.g. polysulfide elastomers), in the production of photographic films and paint removers, and as an insecticidal fumigant and control agent against peach tree borers, Japanese beetles, and root rot nematodes.

The Chemical Economics Handbook (Stanford Research Institute 1972) reported the following U.S. consumption for EDC in 1970:

Ethylene Dichloride Consumption - 1970

Use	Percent
Vinyl chloride	77
Exports	8
Lead scavenger	3
Trichloroethylene	3
Perchloroethylene	3
Methyl chloroform	2
Ethyleneamines	2
Vinylidene chloride	2
Miscellaneous	--

TABLE 4-7

Composition of By-products from Vinyl Chloride Production using the Oxychlorination Process

By-product	Formula	Weight Percent
1,1,2-Trichloroethane	$CHCl_2-CHCl_2$	67
1,2-Dichloroethane (EDC)	CH_2Cl-CH_2Cl	20
1,3-Dichlorobutane	$CH_3CHClCH_2CH_2Cl$	3
1,2-Dichlorobutane	$CH_3CH_2CHClCH_2Cl$	2
1,4-Dichloro-2-butene	$CH_2ClCH=CHCH_2Cl$	2
1,2,4-Trichloro-2-butene	$CH_2ClCH=CClCH_2Cl$	1.1
Pentachloroethane	$CHCl_2CCl_3$	1
Trichloroethylene	$CHCl=CCl_2$	1
asym. Tetrachloroethane	Cl_3CCH_2Cl	1
1,3-Dichloro-2-butene	$CH_3CCl=CHCH_2Cl$	0.5
1,2,4-Trichlorobutane	$CH_2ClCH_2CHClCH_2Cl$	0.3
bis (2-Chloroethylether)	$(CH_2ClCH_2)_2O$	0.3
1,3,4-Trichloro-1-butene	$CH_2ClCHClCH=CHCl$	0.3
1,1,2-Trichlorobutane	$CCl_2CHClCH_2CH_3$	0.3
2,3,4-Trichloro-1-butene	$CH_2ClCHClCCl=CH_2$	0.2
		100.0%

Source: Jensen *et al.* 1970

1,2-Dichloropropane (PDC)

Physical Properties 1,2-Dichloropropane (propylene dichloride, propylene chloride) is a clear, colorless, flammable liquid with a chloroform-like odor. It has the chemical formula $CH_3CHClCH_2Cl$ and a molecular weight of 112.99. It is a solvent for fats, oils, waxes, gums, resins, cellulose esters, and ethers. It is miscible with alcohol, ethyl ether, and most of the common organic solvents including the chlorinated solvents. Its solubility in water is 2600 ppm at 20 C. The following are some of PDC's physical properties:

Boiling point: 96.8 C @ 760 mm Hg

Freezing point: -80 C

Specific gravity: 1.1593 @ 20 C

Vapor density: 3.9 (air = 1.0)

Flash point: 21 C (open cup)

Refractive index: 1.4068 @ 20 C

Vapor pressure:

C°	mm Hg
-6.1	10
19.4	40
25	50
39.4	100
76.0	400

Production PDC is produced by three companies at five sites in the United States (Table 4-8). The annual production of PDC since 1961, when the U.S. Tariff Commission started recording production and sales, is shown on Table 4-9. As of 1970 two companies were producing PDC in the United Kingdom (Chemical Industries Association, Ltd. 1970). PDC can be manufactured by reacting chlorine with propylene.

Consumption PDC is mainly used in the production of carbon tetrachloride and Per. EPA's OHM-TAD System estimates that 85 percent is used as an intermediate in the production of these solvents. It is also used as a solvent (e.g. for oils, fats, waxes, gums), lead scavenger for antiknock fluid, spotting agent, and (when mixed with dichloropropylene) as a soil fumigant. PDC is a principal constituent (30 percent wt/wt) of the pesticide D-D (Vidden D; 1,3-D), which is used as a soil fumigant to combat plant parasitic nematodes and fungi. The total U.S. farm use of D-D was 3.2×10^3 tons in 1971 (Berry 1973, pers. comm.).

TABLE 4-8

United States Producers of 1,2-Dichloropropane and Production Sites

Company[1]	Production Site[2]
The Dow Chemical Corporation	Freeport, Texas Plaquemines, Louisiana
Jefferson Chemical Corporation	Port Neches, Texas
Union Carbide Corporation	Institute & South Charleston, South Carolina

[1] Company list comes from U.S. Tariff Commission 1972 & U.S. Environmental Protection Agency, OHM-TAD, unpublished data.

[2] Production sites come from U.S. Environmental Protection Agency, OHM-TAD, unpublished data.

TABLE 4-9

United States Production and Sales of 1,2-Dichloropropane (PDC)

Year	Number of Manufacturers	Production (Metric Tons)	Sales (Metric Tons)	Reference
1972				
1971	3		11,100	1
1970	3	--	9,876	1
1969	3	--	--	1
1968	3	--	13,800	1
1967	3	39,100	13,000	1
1966	3	34,600	--	1
1965	3	27,600	14,100	1
1964	4	26,500	14,600	1
1963		16,100	12,500	1
1962		16,100	10,800	1
1961		17,100	10,200	1
1960		--	--	
1959		--	--	
1958		--	--	

Source: U.S. Tariff Commission 1962-1973

General Chemical Properties and Reactions

All chlorinated hydrocarbons decompose by oxidation, hydrolysis or pyrolysis (McGovern 1943). Chlorinated olefins are particularly susceptible to oxidation by atmospheric oxygen (Hardie 1964). LMCH's will decompose to smaller fragments when exposed to open flames and very hot surfaces. When thermal decomposition does occur, HCl and Cl_2 are formed (Hama and Curley 1965). Sjoberg (1952), and Crummet and Stenger (1956) have shown that small amounts of phosgene may also be formed during thermal decomposition. The concentration of HCl, however, is many times greater than the concentration of phosgene. Gunewardene (1941) has reported the formation of phosgene, which rapidly decomposes in water, when Per is exposed to strong ultraviolet light. Many of the LMCH's (e.g. 1,1,1-TCE and PDC) can react with aluminum and inhibitors must be added to prevent corrosion.

There is a general progressive change in physical properties with increasing substitution of chlorine atoms on the methane, ethane, and ethylene molecule. Thus, density and viscosity show a progressive increase with increasing chlorine substitution, whereas specific heat, dielectric constant, and solubility in water show a progressive decrease.

Substitution Chlorination

This reaction involves the substitution of chlorine for one or more of the hydrogen atoms of a hydrocarbon; it proceeds by a radical chain mechanism in which the chlorine atom is activated by thermal or photochemical means. Thermal activation involves the dissociation of the chlorine molecule ($Cl_2 \rightleftharpoons 2Cl$) by temperatures above 250 C or by light in the 3000 to 5000 Å wave band. Methane reacts with chlorine at about 400 C in the absence of contact catalysts. The chlorination reaction is strongly exothermic. The average heat of reaction is about 24 kcal/g-mole. These reactions can be promoted by radical-producing catalysts and may have some importance in atmospheric behavior.

Oxidation

Olefins are susceptible to oxidation by molecular oxygen and ozone. When irradiated with UV Per, in the presence of air or oxygen, undergoes autooxidation to trichloroacetyl chloride. An intermediate stage in this reaction is the formation of peroxy compounds which undergo a rearrangement to give trichloroacetyl chloride and oxygen and/or phosgene. Rearrangement to trichloroacetyl chloride predominates. The slow decomposition of Per that takes place on prolonged storage in light and the presence of air is due to this autooxidation reaction (Hardie 1964). Per does not react with oxygen in the dark (Hardie 1964).

Stability

The chlorinated hydrocarbons are stable at room temperature and when in contact with most common construction metals, although many are sold containing small amounts of stabilizing additives to prevent decomposition. Per is thermally and photochemically the most stable of the chlorinated ethylenes. Unstabilized Per, however, slowly decomposes to trichloroacetic acid and hydrochloric acid in the presence of H_2O. In the presence of ozone, Per is decomposed to phosgene and trichloroacetyl chloride. 1,1,1-TCE also decomposes in the presence of water or steam, and in the absence of stabilizing agents, at elevated temperature it is oxidized by the atmosphere (Crummett and Stenger 1956). With respect to phosgene formation, 1,1,1-TCE is one of the more stable chlorinated hydrocarbons (Crummett and Stenger 1956).

EDC is stable to water, acids, and some other active chemicals. In the presence of air, moisture, and light, it undergoes slow decomposition, becomes acidic and darkens in color.

Toxicity to Humans and Higher Animals

The narcotic action of the halogenated hydrocarbons is well recognized and documented. Some of the halogenated hydrocarbons are also known to cause liver dysfunction. Plea and Larson (1965) have shown that of the chlorinated methanes, ethanes, and ethylenes, only $CHCl_3$ and 1,1,2-TCE produce renal dysfunction. The narcotic action occurs by depression of the central nervous system, leading to various stages of anaesthesia and finally, at high exposure, to death. Effects on animal behavior have also been noted (Goldberg *et al.* 1964). A number of the chlorinated hydrocarbons (e.g. chloroform and trichloroethylene) have been used successfully as anaesthetics.

Chlorinated hydrocarbons assimilated by humans may be eliminated by excretion into the pulmonary alveoli and by excretion of the compound or its metabolites through the kidneys. Stewart (1969), Stewart *et al.* (1970), and

Hake *et al.* (1960) suggested that the excretion of solvents from the lungs is closely related to such physical properties as vapor pressure and boiling point. The higher the vapor pressure of the solvent the more quickly it will be excreted through the lungs. The speed of excretion will influence the degree of metabolism by affecting the exposure time of the compound to *in vivo* processes. The LMCH's are only slightly metabolized in humans and are excreted.

When metabolized by animals, the halogenated hydrocarbons, particularly the chlorinated hydrocarbons, degrade by dehalogenation. Heppel and Porterfield (1948) showed that enzymatic dehalogenation occurred in the liver. Bray *et al.* (1952) reported liver extracts which can nonenxymatically liberate the chlorine atom from certain chloromethanes. This apparently was the result of the formation of carbon-sulfur bonds with the loss of the halogen atom which may be replaced either by cysteine or hydroxyl. When the chlorine atom is replaced by cysteine the N-acetylcysteine (mercapturic acid) derivative is excreted in the urine. The hydroxylated derivative is either excreted as such or in the form of its glucuronide (Zitko and Choi 1971). Van Dyke and Wineman (1971) reported that an enzyme system from hepatic microsomes of rabbits, rats, and guinea pigs was capable of dechlorinating chloroethanes and chloropropanes. This system requires NADPH and oxygen and shows considerable substrate specificity; 13.5, 6.0, and 0.5 percent of chlorine were enzymatically removed from 1,1-EDC; sym-tetrachloroethane; and 1,2-EDC, respectively. The removal of chlorine from chloropropanes was 5.8, 24, 3.2, and 40.8 percent for 1,2-PDC; 1,1-PDC; 1-chloropropane; and 1,1,2-trichloropropane, respectively.

Several investigations have indicated that chloroform and carbon tetrachloride are converted to CO_2 *in vivo* and in the presence of liver slices (McCollister *et al.* 1951, Paul and Rubinstein 1963, Van Dyke *et al.* 1963, Lee *et al.* 1964, Rubinstein and Kanics 1964).

Discussions of the toxicity literature on Per, 1,1,1-TCE, EDC, and PDC may be found in the documentation of threshold limit values (TLV's) established by the American Industrial Hygiene Association (1961, 1965a, 1965b, 1967) which are summarized below:

Compound	TLV, ppm
Perchloroethylene	100
Ethylene dichloride	50
Propylene dichloride	75
1,1,1-trichloroethane	350

Routes of Entry into the Environment

Release of LMCH's into the environment generally is attributable to four primary sources: the dispersive use of solvents such as Per and 1,1,1-TCE; leakage during production; disposal of production wastes; and transportation losses. LMCH's may possibly be produced in natural reactions through the breakdown of higher molecular weight chlorinated compounds.

Dispersive Uses

We assume that the only major sources of atmospheric Per and 1,1,1-TCE are dispersive uses. We estimate that approximately 90 percent of the production of Per is released into the environment, primarily the atmosphere. The remaining production is used in the manufacture of fluorocarbons. However some loss of these compounds to sewage plants results from discarding dirty solvent, water-solvent separators, or careless or ineffective handling. Some Per is injected directly into rivers from production sites by plant effluents. We assume a world production rate in 1972 of 10^6 tons, and estimate that 9×10^5 tons/year of Per is released into the lower atmosphere, almost entirely in the Northern Hemisphere, with the points of injection corresponding closely to the population distribution. The injection of Per into natural water systems from dispersive uses is difficult to evaluate. Very few reports mention the detection of Per in sewage plant effluent water.

1,1,1-TCE is used primarily as a cleaning solvent. Thus, like Per, the main introduction is into the atmosphere with small quantities being introduced to sewer systems. We estimate a world production rate of 3.5×10^5

tons per year (U.S. production x 2) and nearly all will be released to the environment.

There are minor dispersive uses of EDC and PDC. EDC is used as a solvent and as a fumigant for grain, pulses, and animal feeds. The 1971 farm usage of EDC was 1.74 x 10^5 tons in the United States (Appendix III), which appears to account for smaller amounts of EDC introduced to the environment than through production loss. PDC is used in a mixture with 1,2-dichloropropane as a soil fumigant. It is injected into the soil at a depth of 8 to 20 inches and normally persists at nematocidal dosages for several days or weeks. The normal dosage is 0.2 l/m^2 for D-D mixture (30 percent wt/wt of 1,2-PDC) (Thomason *et al.* 1971).

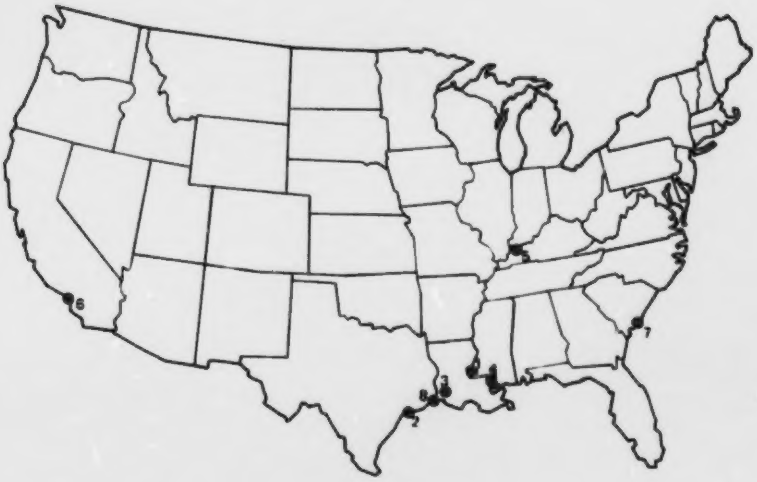
Production Losses

The primary uses of EDC and PDC are for the production of other chlorinated hydrocarbons. The majority of U.S. chlorinated hydrocarbons are produced on the upper Gulf coast (Figure 4-3). Murray and Riley (1973) have estimated that the losses to the environment of compounds which are used as intermediates are unlikely to exceed 1 or 2 percent. Assuming a loss from production of 1.5 percent, we estimate the injection of EDC into the environment on a worldwide basis to be 175 x 10^3 tons/year. PDC is primarily used in the production of CCl_4 and CCl_2=CCl_2. Based on production values, we estimate the release of PDC to the environment from production to be two to three orders of magnitude less than EDC.

The release of LMCH from production plants is hard to evaluate because these compounds are not monitored in plant effluents. However, incidents of production losses have been reported. Lyne and McLachlan (1949) reported 2 incidents in which water from wells near factories which used large amounts of trichloroethylene was rendered unfit for drinking because of contamination resulting from dumping of this liquid.

Dumping and Transportation Losses

Dumping of wastes and loss during transport can be the major source of these compounds in the marine



Production Sites

1. Baton Rouge, Plaquemine, and Geismar, Louisiana (4 plants)
2. Houston, Deer Park, Texas City, Oyster Creek, and Freeport, Texas (6 plants)
3. Lake Charles and Westlake, Louisiana (2 plants)
4. Taft, Louisiana
5. Calvert City, Kentucky
6. Waton, California
7. Institue and South Charleston, South Carolina
8. Port Neches, Texas

FIGURE 4-3

Production Sites of Ethylene Dichloride and Propylene Dichloride environment. Jensen *et al.* (1970) have reported the dumping of EDC-tars into the North and Norwegian Seas. Ocean dumping is discussed in Chapter 5. The composition of these types of by-products for a producer in Louisiana is shown in Table 4-7. The composition of by-products varies widely from producer to producer and perhaps even daily in the same plant. 1,1,2-TCE and EDC are major constituents of these vinyl chloride production wastes.

Both saturated and unsaturated chlorinated ethane, propane, and butane derivatives are being discharged to the ocean. The magnitude of this discharge of LMCH's is unknown. Jensen *et al.* (1970) reported, ". . .high densities of particles were observed, and in some areas the sea was colored red-white by the particles," in the North Sea. The red-white particles were identified as dead plankton with EDC-tars attached. Greve (1971) reported that PDC comprised 60 percent of the contents of 54 of the barrels obtained during Dutch fishing operations or washed ashore along the Dutch coast. Samples from barrels in Rotterdam Harbor were also analyzed. The barrels were bound for dumping in the Atlantic Ocean above 65° at a minimum depth of 2000 m and at least 161 km from the coast. Similar barrels, however, were found in the North Sea and PDC was also a principal constituent of these. Greve (1971) estimated that 650 tons of barrels with a 60 percent PDC content were in Rotterdam Harbor scheduled for ocean dumping.

Chlorinated hydrocarbons also enter the environment from intentional and unintentional discharges during transportation. The EPA's OHM-TAD System gives the following breakdown on bulk transport of most of the LMCH's:

Rail transport:	40.3 percent
Barge transport:	47.8 percent
Truck transport:	11.9 percent

The quantity of these compounds discharged from domestic transport is difficult to evaluate. Losses occur almost inevitably from loading and transfer operations and accidents. Table 4-10 shows the estimated loss from ocean tankers.

A single report has been filed with EPA regarding the spillage of the four chlorinated solvents we investigated. During product synthesis, an unknown quantity of Per and trichloroethylene was spilled by Pittsburg Plate Glass Industries because of the chemical explosion of a reactor (U.S. Environmental Protection Agency, OHM-TAD, unpublished data).

TABLE 4-10

Loss of Synthetic Organic Chemicals from Ocean Tankers (Amount of Cargo Residues Discharged at Sea - 1970)

Compound	Total Amount Shipped (tons)	Amount Left on Board (tons)
Trichloroethane	4,618	5
Dichloropropane	6,685	unknown
Perchloroethylene	39,986	36
Ethylene Dichloride	241,356	80
Benzene	279,852	241
Toluene	366,441	234
Acrylonitrile	93,453	41

Source: Intergovernmental Maritime Consultative Organization, hereinafter referred to as IMCO, 1973

Levels in the Environment

There have been very few reports of concentrations of LMCH's in the environment. The levels observed appear to be low, and special analytical techniques are required to obtain reliable data. Most of the available reports concern atmospheric concentrations in metropolitan areas, and seem to indicate that some of the LMCH's (e.g. CCl_4 and CCl_2=CCl_2) are distributed in the atmosphere. The few reports on concentrations in aquatic environments indicate that these compounds occur in major river systems and in the ocean. Jensen *et al.* (1970) report a wide distribution of LMCH's in the Atlantic Ocean. LMCH's have also been found in sewage sludge (Montgomery and Conlon 1967), and in groundwater after spills (Middleton and Walton 1961).

Williams (1965) reported the detection of CCl_4 and Per at less than 1 ppb in air samples near Vancouver, Canada. These samples were taken to the west of the city limits "in a location where one would expect relatively few atmospheric pollutants."

Lovelock *et al.* (1973) reported that CCl_3F, methyl iodide (CH_3I) and carbon tetrachloride (CCL_4), appear to be distributed in the atmosphere and the sea at less than 1 ppb by volume. The proposed source of CCl3F was propellant solvents used in aerosol sprays, while that of CH_3I was biological methylation in the sea. The latter was based on the ability of algae to produce methyl iodide, and on the larger concentrations in the sea compared with the atmosphere than expected on the basis of its vapor pressure. They also suggested that CCl_4 was a natural product, possibly from the reaction of methane in the troposphere with chlorine in a complex sequence of reactions. They found no large gradient between the northern and southern hemispheres, and calculated an annual production rate for CCl_4 of 1.9×10^6 tons, based on residence time, which is far above the amount any industrial source could contribute. This would seem to confirm a natural source of CCl_4.

Murray and Riley (1973) have reported the detection of $CHCl_3$, CCl_4, trichloroethylene, and Per in rural areas of Britain, and over the northeastern Atlantic (Table 4-11). In all instances, these were the principal chlorinated hydrocarbons detected. Smaller amounts of dichlorodifluoromethane, trichlorofluoromethane, and 1,1,1-TCE were identified. In general, the concentration ranges for these compounds over the sea are similar to those over the land away from urban areas (Table 4-11). In air samples in Liverpool, England, Murray and Riley (1973)

TABLE 4-11

Concentrations of Chlorinated Aliphatic Hydrocarbons in Air (ng/m^3)

Sampling locations							
Land stations							
Date	Lat.	Long.	Wind direction	$CHCl_4$	CCl_4	$CHCl{-}CCl_2$	$CCl_2{=}CCl_2$
	51°10'N	04°20'W	200°	4	0.3	28	17
	53°07'N	04°07'W	220°	6	0.4	15	57
	53°03'N	04°02'W	240°	2	0.7	2	8
	58°05'N	03°50'W	220°	--	0.3	4	--
	53°14'N	03°38'W	220°	2	0.5	4	13
			Average	4	0.4	11	19
Sea stations							
16.7.72	34°19'N	13°32'W	310°	--	0.2	1	3
17.7.72	30°04'N	12°26'W	030°	0.8	0.3	1	8
18.7.72	27°19'N	13°43'W	040°	1.0	0.2	4	2
20.7.72	26°16'N	14°32'W	035°	0.7	0.3	7	2
27.7.72	20°49'N	17°16'W	360°	1.6	0.7	4	7
8.8.72	26°24'N	14°48'W	002°	1.8	0.4	16	3
16.8.72	34°29'N	14°19'W	356°	1.3	0.3	1	1
20.8.72	43°30'N	09°16'W	340°	1.0	0.2	2	5
21.8.72	48°16'N	06°48'W	355°	3.0	0.2	4	1
21.8.72	49°26'N	06°03'W	355°	4.7	0.4	4	9
21.8.72	49°54'N	05°54'W	005°	--	0.6	22	9
			Average	1.7	0.3	6	5

Source: Murray and Riley 1973

found 3.8 ppt (parts per trillion) $CHCl_3$, 0.4 ppt CCl_4, 160 ppt trichloroethylene, and 1 ppt Per.

Jensen *et al.* (1970) provide the major source of information on the occurrence of LMCH's in the ocean. They reported concentrations of C-Cl for two stations in the Atlantic Ocean and the North Sea. Station 710 (57°N, 4°18'E) showed the highest concentration of 0.2 ppm (parts per million) by weight. The five main gas chromatographic peaks corresponded to those obtained from the by-products in vinyl chloride production. They also reported a C-Cl concentration of 0.6 ppb (by weight) for a water sample taken close to Iceland and a wide distribution of C-Cl from samples from the Barents Sea and Atlantic Ocean. Jensen *et al.* (1970) suggested that the presence of C-Cl in the North Sea, Norwegian Sea and the Irminger Current strongly indicates that C-Cl originates from the industries on both sides of the Atlantic. They also reported C-Cl in subsurface water and the variation of the component concentrations with depth. These changes could be either chemically or biologically induced.

Murray and Riley (1973) reported concentrations of four chlorinated hydrocarbons in North-East Atlantic Surface Water (Table 4-12). Small amounts of dichloro difluoromethane were also detected (~2 μg/I). The smaller ratio of Per relative to the other LMCH's may be due to its more rapid photolysis or possibly to hydrolysis or biodegradation.

Environmental Science and Technology (Anonymous 1973) reported that an EPA lab and a private company had identified five LMCH's in the waters of the lower Mississippi River. The compounds, chloroform, EDC, methyl chloride, 1,1,1-TCE, and Per, were detected in trace amounts by collection on activated charcoal. Nine halogenated hydrocarbons have been detected in Louisiana finished and raw water (U.S. Environmental Protection Agency 1972) (Table 4-13).

Montgomery and Conlon (1967) reported chloroform (0.02 to 0.03 mg/l), carbon tetrachloride (0.1 to 0.2 mg/l), trichloroethylene (0.03 to 0.3 mg/l), and 1,1,2-trichloro-1,2,2-trifluoroethane (0.02 to 0.05 mg/l) in crude and digested sludge in England. Kleopfer and Fairless (1972) detected 4 light halogenated hydrocarbons (bromodichloromethane, chlorodibromomethane, Per, and

TABLE 4-12

Concentrations of Some Chlorinated Hydrocarbons in the Northeastern Atlantic Surface Waters (ng/l)

Sample No.	Lat.	Long.	Temp. (°C)	Salinity (%)	$CHCl_3$	CCl_4	$CHCl\text{-}CCl_2$	$CCl_2{=}CCl_2$
A 37	26°14'N	14°53'W	21.0	36.54	4	0.12	7	0.2
A 46	26°09'N	14°46'W	20.4	36.51	8	0.15	10	0.2
A 47	26°07'N	14°50'W	20.9	36.58	8	0.17	--	0.8
B 12	26°21'N	14°50'W	21.5	36.73	13	0.12	5	0.6
B 13	26°10'N	14°56'W	21.3	36.62	9	0.26	8	0.4
B 14	26°15'N	14°38'W	13.6	26.26	8	0.21	11	0.7
Average					8	0.14	7	0.5

Source: Murray and Riley 1973

TABLE 4-13

Chlorinated Hydrocarbons in Water Supplies in Louisiana

Organic Compound	Carrollton Finished Water	P.H.S. Hospital Finished Water	Jefferson Parish #2 Raw Water
ethylene dichloride		X	
tromoform	X		
carbon tetrachloride		X	
chloroform	X	X	
dichlorobutene			X
1,2-dichloroethane	X	X	
methyl chloride	X	X	
tetrachloroethylene	X		
1,1,2-trichloroethane	X		

Source: U.S. Environmental Protection Agency 1972 bromoform) in the municipal drinking water of Evansville, Indiana, the source of which is the Ohio River. These analyses were performed by absorption on activated carbon filters, and no absolute concentrations were reported. Novak *et al.* (1973) have found five halogenated hydrocarbons in Prague drinking water. Chloroform was detected at 9.1 x 10^{-4} mg/l, EDC and CCl_4 at less than 10^{-4} mg/l, and Per and trichloroethylene at trace levels.

Hood *et al.* (1958) reported organic chloride from marine sediments in the vicinity of dumping by Shell Chemical Corporation in the Gulf of Mexico.

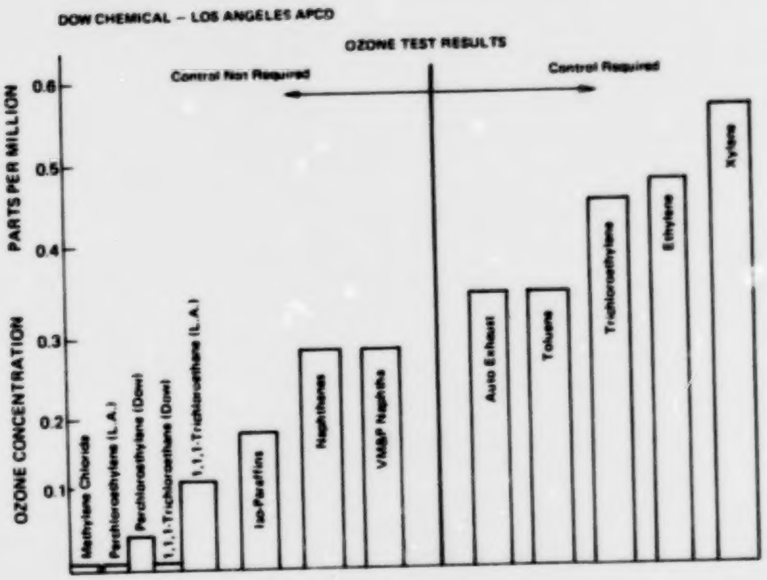
Fate in the Environment

Fate in Atmosphere

The chlorinated hydrocarbons exhibit different rates of chemical reaction in the atmosphere. This has been recognized for several years and has had an effect on the production of chlorinated solvents in the chemical industry. Recognition that trichloroethylene produces oxidants when exposed to simulated sunlight has led to an increase in the use of other more stable chlorinated solvents as replacements. The amount of oxidant formed in simulated sunlight is approximately inversely proportional to the stability of the parent compounds in the atmosphere. The more stable chlorinated solvents (e.g., Per and 1,1,1-TCE) produce small quantities of oxidant compared with trichloroethylene, which rapidly disappears when exposed to simulated sunlight. The Los Angeles APCD's test results are shown in Figure 4-4 along with those of Dow Chemical U.S.A. (Farber 1973, unpub. ms.). Because of these findings, legislation (Rule 66) for the abatement of photochemically reactive solvents resulted in Los Angeles. Altshuller *et al.* (1971) have also reviewed the photochemical properties of these solvents. They found that Per and the saturated chlorinated hydrocarbons were virtually unreactive. They cited an unpublished work by Kopezynski, which reported that trichloroethylene has a half life of 157 minutes in the lower atmosphere. Hamming (1967) has reported that Per has a low potential for photochemical smog formation.

The primary discrepancy in Figure 4-4 is between the generation of oxidant from trichloroethane and Per. Dow

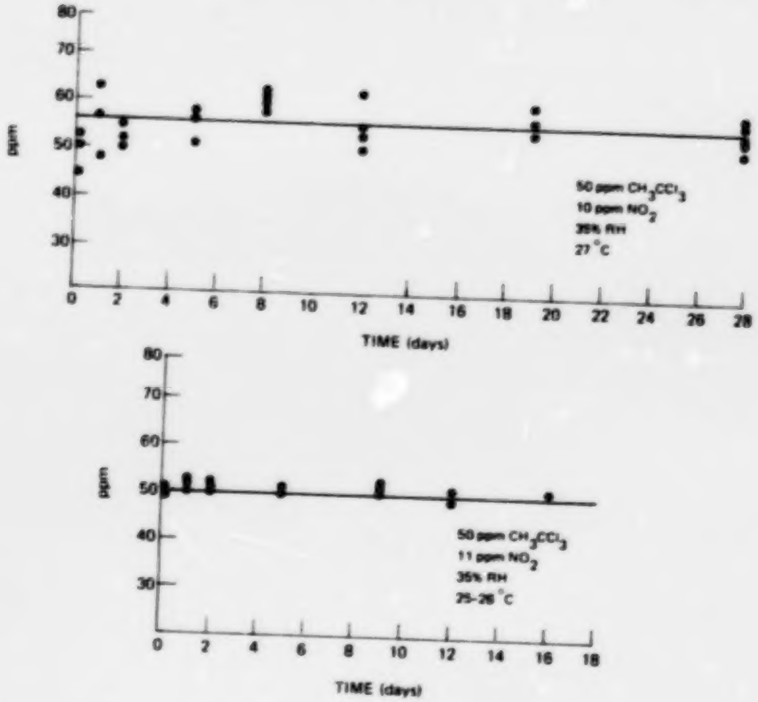
Chemical, USA scientists found that Per was more reactive than 1,1,1-TCE which is contradictory to the earlier findings of Los Angeles APCD (Figures 4-5, 4-6, Table 4-14).



Source: Farber 1973, unpublished ms.

FIGURE 4-4

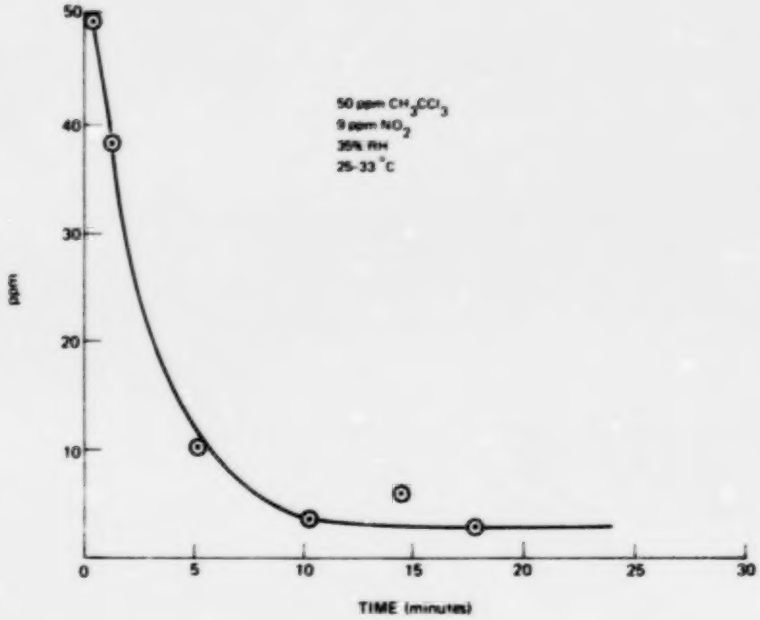
Photoreactivity Oxidant Generated in Smog Chambers



Source: Dow Chemical USA 1973 pers. comm.

FIGURE 4-5

Simulated Sea Level Irradiation of 1,1,1-Trichloroethane



Source: Dow Chemical USA pers. comm.

FIGURE 4-6

High Altitude Photoreactions of 1,1,1-Trichloroethane

TABLE 4-14

Reactivity of Two Chlorinated Hydrocarbons in the Presence of NO At Various Concentrations

Compound	Initial Concentration (ppm) Compound/NO	Reactivity (based on disappearance of the material)	Relative Rate
$CCl_2{=}CCl_2$	10/5	29% @ 6-1/2 hr.	1.0
	40/20	50% @ 7 hr.	1.6
	100/50	50% @ 3-3/4 hr.	3.0
$CHCl{=}CCl_2$			
$CHCl{=}CCl_2$	10/5	50% @ 3-1/2hr.	1.0
	20/10	50% @ 3 hr.	1.2
	40/20	50% @ 1-1/2 hr.	2.3
	100/50	50% @ 1 hr.	3.5

Source: Dow Chemical Company USA 1973 pers. comm.

An experiment to obtain sea level irradiation data for 1,1,1-TCE (Figure 4-5) was performed using two GE RS-275W sunlamps with an intensity of 1 to 2 times that of noontime sea level sunlight at wavelengths greater than 295 mμ. The 1,1,1-TCE was analyzed by gas chromatography and was found to be stable in both experiments at simulated sea level conditions. Figure 4-6 shows the irradiation of 1,1,1-TCE at simulated high-altitude conditions. The high-altitude radiation was provided by a Hanovia low-pressure mercury arc lamp. This lamp emitted approximately 90 percent of its radiant energy at 2537 Å which is 10 to 40 times as intense as the sun's radiation just outside the earth's atmosphere and would be 30 to 120 times as intense as sunlight at an altitude of 40 km. The irradiated atmosphere contained 9 ppm NO_2, 50 ppm of 1,1,1-TCE, and had a relative humidity of 35 percent at 25 C to 33 C. Under these simulated high-altitude conditions 94 percent of the 1,1,1-TCE was decomposed within 10 minutes. The residual amount (3 ppm) was thought to be an artifact of the system caused by absorption of 1,1,1-TCE on surfaces (e.g. rubber septa). The simulated high-altitude irradiation was also performed using an NO_2-free atmosphere and a moisture-free atmosphere. Using an NO_2-free atmosphere, the 1,1,1-TCE appeared to be almost completely gone in 6 minutes. In 10 minutes, 1,1,1-TCE was 92 percent decomposed in a water-free 50 ppm 1,1,1-TCE mixture at 24 C to 33 C. Scientists at Dow Chemical, USA, also reported that there was no decrease in the concentration of 1,1,1-TCE after 4 days in the dark in the presence of pure ozone. These results indicate that 1,1,1-TCE is fairly nonreactive in sea-level atmospheres but as it is mixed upward its photochemical decomposition will increase. Dow Chemical, USA, researchers (Table 4-14) used GE RS-275 watt sunlamps to irradiate a sample containing Per for 6 to 8 hours, approximating 2 or 3 days of intense noontime sun for 6 hours each day. Per was susceptible to photochemical decomposition at these simulated sea-level conditions. Table 4-14 also shows the photochemical reactivity with change in concentration of Per and 1,1,1-TCE and NO at 35 to 40 percent relative humidity.

Several literature reports on the breakdown products of the LMCH's under various conditions of light, O_2, Cl_2, and water are available. The data in these reports are difficult to apply because they involve unnatural atmospheric conditions, or involve concentrations considerably higher than those found in the atmosphere. Frankel *et al.* (1957) reported on the photochemical oxidation of Per in the presence of oxygen and excess chlorine at 36 to 40 C. When this mixture was exposed to sunlight for 12 hours trichloroacetyl chloride (40 percent), tetrachloroethylene oxide (9 percent), hexachloroethane (8 percent), and phosgene were obtained. The remainder of the mixture was unreacted Per.

Bailey and Hickson (1941) reported formation of trichloroacetic acid after exposure of Per and water to sunlight in the liquid phase. They postulated that the oxidizing agent may be O_3 or H_2O_2 formed photochemically. Several other investigators have reported the formation of $COCl_2$, CCl_3COCl, the epoxide, and CCl_3CO_2H under varying conditions of H_2O, O_2 and H^- (Müller and Ehrmann 1936, Rushmer and Smith 1947, and Yasnitskii *et al.* 1963).

Hardie (1964) reported the autooxidation of Per to $CHCl_2COCl$ and $COCl_2$ in the presence of O_2, and accelerated by high temperature and light.

Fate in Aqueous Environments

Evaporation, chemical hydrolysis, and biological degradation are potential processes for the removal of chlorinated hydrocarbons from aqueous systems. Evaporation occurs in systems with strong turbulent mixing. Chemical hydrolysis in the presence or absence of light can decompose these substances.

Evaporation Rate In strongly mixed aqueous systems, half-lives of LMCH's are on the order of minutes as compared to half-lives from biological degradation or hydrolysis which are on the order of days and months, respectively. MacKay and Wolkoff (1973) have calculated the rate of evaporation from aqueous solutions of compounds such as hydrocarbons and chlorinated hydrocarbons which have low solubility. Benzene, for example, partitions 62 percent to the vapor phase when 0.01 percent of the water has evaporated. A problem with their approach is that there are very few aqueous systems in which the turbulent mixing is fast enough to keep the surface boundary concentrations equal to the bulk of the solution. In this case, the overall rate of loss across the interface is controlled by diffusion or mixing.

Dow Chemical, USA, also determined evaporation rates for Per, trichloroethylene, and 1,1,1-TCE in the presence of a 2.2 mph wind, 500 ppm wet Bentonite, 500 ppm peat moss and 30,000 ppm salt (Table 4-15). The experiments were carried out in a 250 ml beaker with 200 ml of 1 ppm solution and stirred with a magnetic stirring bar at 200 rpm. The variation in evaporation rates were less than a factor of 2 for all these conditions. The data seem to indicate that sorption of the compounds tested onto these particulates may not be significant.

Chemical Degradation The LMCH's can degrade by chemical hydrolysis. Hardie (1964) reported that Per undergoes hydrolysis slowly in the presence of water. Shepherd (1962) reported a hydrolysis rate for Per in the absence of air and metals of 0.01 mg/l/day at 25 C.

TABLE 4-15

Evaporation of Chlorinated Hydrocarbons Under Various Conditions

Condition	Time (min) for 50% disappearance		
	$CCl_2=CCl_2$	$CHCl=CCl_2$	CH_3CCl_3
Tap water @ 25°	24	22	22
Tap water @ 1-2°	42	37	33
3% Salt Solution	28	25	25
~500 ppm Peat Moss	21	20	20
~500 ppm Wet Bentonite Clay	20	20	20
2.2 mph Wind	19	17	17

(Conditions: 250 ml beaker with 200 ml water with 1 ppm solute initially at 25°. Stirred at 200 rpm.)

Dow Chemical, USA, researchers calculated half-lives for a number of LMCH's in water containing air under dark and light conditions (Table 4-16). The experiments were performed by sealing a 1 ppm solution of the compound in a Pyrex tube (for dark experiments) or a quartz tube (for light experiments). The solution occupied 28 percent of the volume in the quartz tubes and 51 percent of the volume in the Pyrex tubes. The Pyrex tubes were placed in a light-proof container and the quartz tubes on the roof of a building in Midland, Michigan. The analysis of solvent from tubes was made using mass spectrometry. They found that 1,1,1-TCE has the same reaction rate in dark and light. This is consistent with atmospheric photolysis results which indicated it was unreactive when exposed to sea-level light. Per decomposed more rapidly in light.

TABLE 4-16

Decomposition Rates of Chlorinated Hydrocarbons in Aerated Water in the Dark and in the Presence of Sunlight

Compound	Initial Concentration (ppm)	6 Months (ppm)	12 Months (ppm)	t 1/2[c] (months)
CCl_2=CCl_2				
Dark[a]	1.00	0.63	0.35,0.41	9
Light[b]	1.00	0.52	0.24,0.25	6
CH_3CCl_3				
Dark[a]	1.00	0.46	0.26,0.29	6
Light[b]	1.00	0.46	0.32,0.25	6
CHCl=CCl_2				
Dark[a]	1.00	0.68	0.44,0.48	11
Light[b]	1.00	0.56	0.21,0.30	6
CH_2Cl_2				
Dark[a]	1.00	0.76	0.68,0.70	22
Light[b]	1.00	0.79	0.64,0.64	18
$CHCl_3$				
Dark[a]	1.00	0.73	0.63,0.65	18
Light[b]	1.00	0.75	0.56,0.57	15

[a] Temperature 25 C (room temperature)
[b] Temperature range -20 to +40 C
[c] Calculated assuming a first order reaction

Source: Dow Chemical, USA. 1973, pers. comm.

Jensen *et al.* (1970) reported that the C-Cl concentration from EDC-tar remained unchanged for 27 days at room temperature in water with no biological activity.

Biological Degradation Several biological oxygen demands (BOD) are reported in the literature for the LMCH's. Dow Chemical, USA, found that 1,1,1-TCE, tetrachloroethane, EDC, PDC and Per did not show a BOD in 20 days. Mills and Stack (1954) reported a 10-day BOD at 20 C for EDC of 0.05 equivalents (theoretical BOD of 1.0 equivalents) using aeration and a dispersed seed originally developed from settled sewage. Ilisescu (1971) has reported that PDC is degradable by adapted microorganisms. Jensen *et al.* (1970) showed that the five major components of EDC-tar degraded in the presence of *Calanus finmarchinous* at 4 to 9 C in 9 days, with degradation varying from 100 to 30 percent in 9 days.

Fate in Soils

For 15 to 25 years polyhalo-organic compounds have been used as biocides in agriculture. They are generally injected into well-tilled, moist soils to depths of 8 to 20 inches. They persist at effective dosages for several weeks (Thomason *et al.* 1971).

Castro *et al.* have investigated hydrolysis and degradation of haloorganic compounds in soils (Castro and Bartnicki 1965, 1968; Belser and Castro 1971; Thomason *et al.* 1971). Using neutron activation methods they reported no organic halides present in food crops grown on soil treated with ethylene dibromide (EDB), 1,2-dibromo-3-chloropropane (DBCP), and 1,3-dichloropropene (1,3-D). Increased amounts of inorganic bromide and chloride ion were found in the plants. The haloorganics were rapidly lost from the soil, and had little or no tendency to bioaccumulate.

The increase in total inorganic bromine and chlorine content of some plants grown on EDB, BDCP and 1,3-D treated soils indicates that these compounds break down to simple molecules or ions. Castro and Belser (1966) found that cis- and trans-1,3-dichloropropene are chemically hydrolyzed in moist soil to the corresponding 3-chloroallyl alcohol which is biocidal. The hydrolysis occurs biologically and chemically in water buffered systems and oil-solution mixtures. The chemical hydrolysis apparently was more important because the rate of halide release was relatively insensitive to the amount of soil present. Belser and Castro (1971) observed that 3-chloroallyl alcohol was metabolized to carbon dioxide and water by a bacterium (*Pseudomonas*) isolated from soil. The 3-chloroallyl alcohol is first converted to 3-chloroacrylic acid, the chlorine is then removed from the molecule, and the intermediate products are converted to CO_2 and water. Their kinetic studies indicated a low steady state concentration of intermediates. Decarboxylation and conversion to CO_2 was not studied but it occurs in other organisms. If this occurs under field conditions, then there would be little possibility of the transfer of residues to the oceans.

Castro and Belser (1968) indicate that EDB and DBCP undergo geological dehalogenation but are more resistant to chemical hydrolysis. Under laboratory conditions DBCP is converted to n-propanol. The resulting allyl chloride from DBCP debromination would probably hydrolyze even nonenzymatically to n-propanol (Castro and Belser 1966). The maximum conversion of DBCP to n-propanol was 63 percent complete in 4 weeks. EDB is converted almost completely in two months to ethylene by reductive dehalogenation. Dibromobutanes also showed dehalogenation, but only under conditions that supported growth and only when the substrate was present during the growth phase of the soil bacteria.

These kinds of hydrolyses and dehalogenations would be expected to occur with Per, EDC, 1,1,1-TCE, and PDC which find their way into the soil. These same reactions might also be found in aqueous environments.

Effects on Ecosystems

The effects of LMCH's on aquatic ecosystems are poorly understood. Most of the published literature consists of studies of acute exposure to selected LMCH's, or sketchy data on the effects of EDC-tars on marine species. The LMCH's seem to have a low potential for bioaccumulation in aquatic systems, although they have been reported in aquatic organisms. The acute toxicity reported for most of the LMCH's is in the lower parts per million range.

There have been relatively few reports on the acute toxicity of the LMCH's on aquatic organisms. Garrett

(1957) reported acute 48-hour toxicity of some chlorinated solvents (Table 4-17). Union Carbide Corporation scientists (Lane 1973, pers. comm.) reported on EDC LC_{50} using fathead minnows of 500 ppm or greater. Applegate *et al.* (1957) reported that 5 ppm of EDC for 24 hours had no effect on rainbow trout (*Salmo gairdeneri*) and bluegill sunfish (*Lepomis macrochirus*). Appendix II lists maximum safe and 100 percent of LMCH kill levels for fish (Dow Chemical, USA, 1973 pers. comm.). Aleksandrova (1962), in investigations of sewage treatment operations, reported that CH_2Cl_2 was harmless to flagellates and infusoria in concentrations up to 2,000 mg/l and to nitrifiers up to 250 mg/l.

The toxicity of trichloroacetic acid (TCA), a breakdown product of some of the LMCH's, is quite low. Chancellor (1958) has reported that fish and the organisms on which they feed can tolerate TCA at concentrations of 1.15 percent. The 96-hour TL_m at 20 C for fingerling channel catfish is greater than g/l, and there was no mortality of chinook salmon at 870 mg/l (McKee and Wolf 1963).

There have been several reports of the toxicity of the EDC-tars to marine organisms. Jensen *et al.* (1970) observed that there were high concentrations of C-Cl, dead plankton, and fish in "bad condition" at station 710 in the North Sea. Using C^{14} productivity methods (Steeman Nielsen 1952), Jensen *et al.* (1970) reported 50 percent reduction in C^{14} uptake at about 13 ppm by C-Cl from the oxychlorination process. The plankton samples were incubated for 1,2,3, and 4 hours before the tracer was added. At the lowest concentration tested, there was an apparent activation of the photosynthesis of *Dunaliella sp.* Jensen *et al.* (1970) confirmed this finding using algae samples from Oslo Fjord, Sweden.

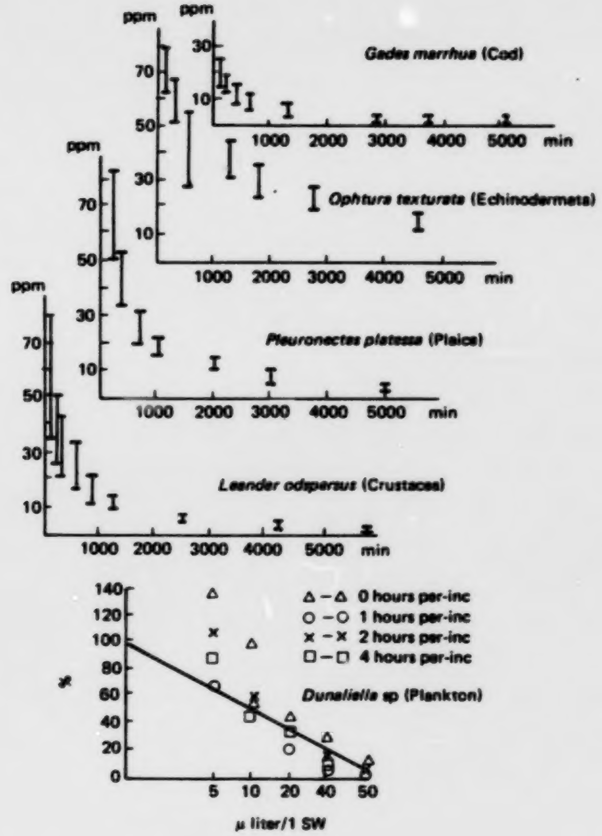
The effect of varying concentrations of C-Cl on a plankton species (*Dunaliella sp.*), and the variation of C-Cl LD_{50}'s with time for four marine species have been reported (Figure 4-7). The lowest concentration giving rise to an immediate effect in cod and crustacea (about 2 ppm) is an order of magnitude higher than the highest C-Cl concentration sampled at Station 710 in the North Sea (Jensen *et al.* 1970).

TABLE 4-17

Toxicity Levels of Some Chlorinated Solvents Using Pinperch (*Lagodon Rhomeboides*)

Compound	Concentration at Less Than One-Half Deaths, mg/l	Concentration at More than One-Half Deaths, mg/l
1,2-Dichloroethane	150	175
1,1-Dichloroethane	250	275
1,1,2-Trichloroethane	150	175
1,1,1-Trichloroethane	75	100

Source: Garrett 1957



Source: Jensen *et al.* 1970

FIGURE 4-7

Toxicity Curves for C-Cl on Four Species of Marine Animals and the Effect on the Photosynthetic Activity of *Dunaliella Sp.*

Rosenberg (1972) reported a reduction in the swimming activity of the Stage II nauplii of *Balanus balanoides* at an EDC-tar concentration of 2 ppm. Stage V and VI nauplii were affected at approximately 4 ppm. Newly-settled 2 to 3 week old barnacles showed about a ten times greater tolerance for EDC-tar than did the Stage II *B. balanoides* nauplii. The juvenile *B. balanoides* survived in concentrations of less than 5 ppm for 20 days (Table 4-18). Hood *et al.* (1958) studied the effects of chlorinated hydrocarbons dumped in the Gulf of Mexico. The waste largely contained chlorinated hydrocarbons plus smaller amounts of butyl alcohol. The threshold toxicity level, determined by the effect of the waste on photosynthesis using the light and dark bottle techniques, for the four organisms studied (*Chlamydomonas* sp., *Phorphyridium cruentum*, *Nitzschia* sp., and an unidentified diatom) occurred at about 0.001 percent, whereas the acute toxicity was about 1 percent of saturation (roughly 0.5 ppm).

The bioaccumulation of LMCH's in marine organisms is quite low compared to bioaccumulation exhibited by vertebrates for some of the high molecular weight chlorinated pesticides and other compounds (e.g., PCB and HCB) (Dow Chemical USA 1973, pers. comm.). Calculated and experimentally obtained bioaccumulations in the flesh of rainbow trout of four LMCH's solvents (PCB, HCB, and two unnamed hydrocarbons) have been reported (Figure 4-8).

Brosier *et al.* (1972, unpublished ms.) investigated the bioconcentration and clearance of carbon tetrachloride in rainbow trout (*Salmo gairdeneri*). They found bioaccumulation factors of 17.4 ± 6.5 in the flesh at concentrations of 79 and 720 ppb CCl_4 in water respectively. This indicates the bioaccumulation factor is determined by the partition of the compound between the water and the tissues of the organisms. The bioaccumulation factor for carbon tetrachloride was approximately 62 for the carcass minus flesh, and approximately 39 for the whole fish at both 79 ppb and 720 ppb.

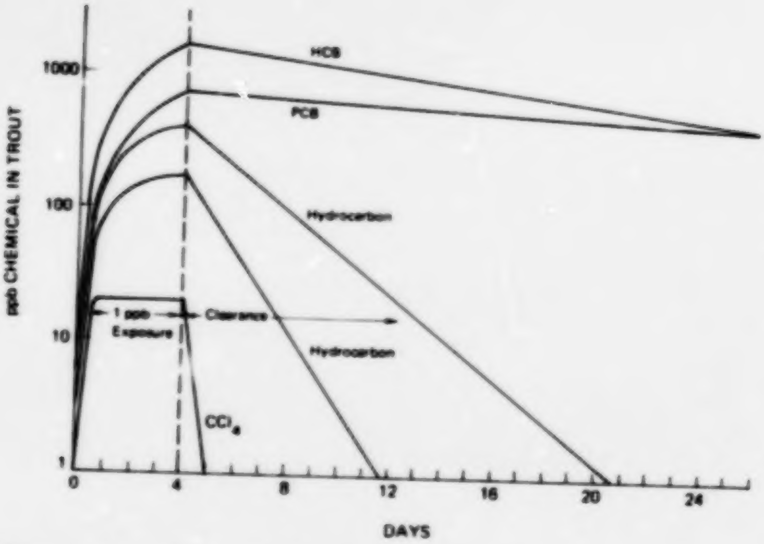
Figure 4-8 shows the rate of uptake and clearance of HCB, 2,2', 4,4' - tetrachlorobiphenyl (labelled PCB), CCl_4 and two hydrocarbons. Trout exposed to a 1 ppb solution of carbon tetrachloride rapidly reach a steady state level of 17 ppb of CCl_4 in flesh. The steady state condition was reached in flesh after 26 hours and in carcass minus flesh after 39+ hours. When fish were

TABLE 4-18

Percentage of Settled Juvenile *Balanus Balanoidea* Surviving 20 Days of Exposure to Different Concentrations of EDC-TAR

EDC-tar (ppm)	0	1	2	5	10	25	50	100
Survival (%)	100	95	100	100	45	6	0	0
No. of juveniles tested	56	76	48	70	72	54	43	46

Source: Rosenberg 1972



Source: Dow Chemical USA, to be published

FIGURE 4-8

Simulated Uptake & Clearance of Chemicals in Trout placed in freshwater the carbon tetrachloride was rapidly cleared. A similar set of experiments performed with Per showed a bioconcentration factor of 40 in flesh (Dow Chemical USA 1973, pers. comm.).

Scientists at Dow Chemical, USA, (to be published) found the log of bioaccumulation linearly related to the log of the partition coefficient between octanol and water for a number of compounds (Figure 4-9). This relationship offers a method of estimating bioaccumulation. Leo *et al.* (1971) tabulated a large number of partition coefficients for different compounds and offered methods for estimating the partition coefficient for other compounds based on structure. The partition coefficient used in these calculations is between water and octanol. Bioaccumulation of PDC, EDC, and 1,1,1-TCE were estimated to be 17, 9, and 13, respectively. These compounds would be expected to act similarly to CCl_4 in organisms, exhibiting rapid uptake to steady state concentration, and rapid clearance.

Murray and Riley (1973) reported the detection of $CHCl_3$, CCl_4, Per, trichloroethylene, and hexachloroethane (0.1 ppm) in mollusks around Port Erin, Isle of Man, where the waters are reported to be "relatively unpolluted".

Tentative Environmental Transport Model for Perchloroethylene

A preliminary mass flow calculation for Per suggests the major routes of transport and degradation, and indicates some unsolved problems. We assume that the mean atmospheric concentration of 5 to 20 ng/m^3 listed in Table 4-11 can be extrapolated to the entire Northern Hemisphere, thus, the total atmospheric load could be of the order of 10^4 tons. Comparing this to our estimated flux to the atmosphere of 9×10^5 tons/year (Table 4-19), the mean residence time in the atmosphere would be of the order of 4 days.* This is in reasonable agreement with the data quoted above on photolytic degradation in the

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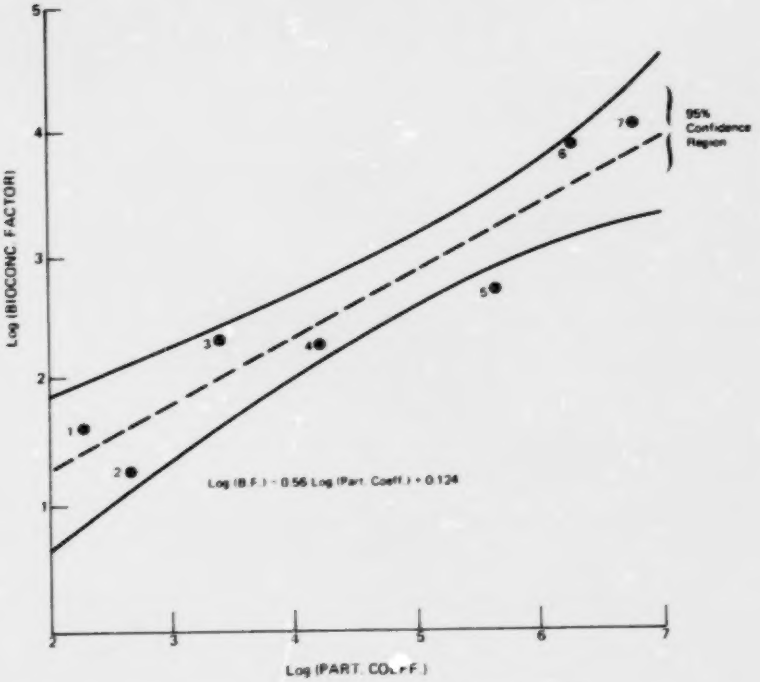
*Residence time is defined here as the ratio between the steady state concentration and the rate of throughput. It is about 1.5 times the half-life for decay in concentration after the input is cut off.



Source: Dow Chemical USA, to be published

FIGURE 4-9

Relationship between Partition Coefficient and the Potential of Chemicals to Accumulate in Trout Muscle

TABLE 4-19

Chlorinated Hydrocarbons Introduced Into the Environment

Hydrocarbon	Atmosphere (Metric Tons)	Hydrosphere (Metric Tons)	Lithosphere (Metric Tons)
Perchloro-ethylene	900,00[1]	100,00[1]	
Ethylene dichloride	175,000[5]		174[4]
1,1,1-Tri-chloroethane	315,000[2]	35,000[2]	negligible
Propylene dichloride			960[3]

[1] Assuming world production rate of 1 million metric tons (1972) and 90% loss to atmosphere and 10% loss to hydrosphere.

[2] Assuming work production rate of 350 million metric tons (1971) and 90% loss to atmosphere and 10% loss to hydrosphere.

[3] From U.S. farm useage in 1971 of D-D (30% PDC). This is only U.S. introduction of this compound into environment.

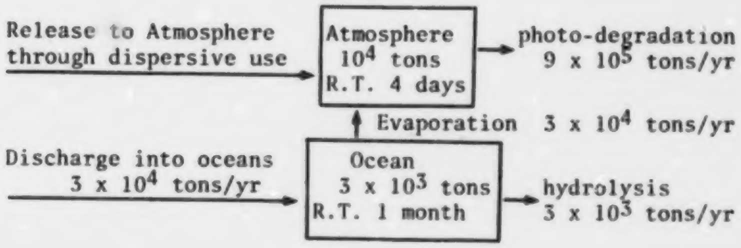
[4] From U.S. farm useage in 1971. Not a world introduction figure.

[5] This is based on a loss from production of 1.5%

atmosphere (pp. 4-46 to 4-53). It is also in reasonable agreement with the mean ratio of 4 between concentrations over land and ocean indicated in Table 4-11 assuming a time scale of the order of a week for transport from terrestrial sources to the oceanic atmosphere.

The mean concentration of 0.5 ng/l quoted in Table 4-12 for surface waters in the North Atlantic (about 3×10^{-9} times the solubility) appears far too high to be in equilibrium with the atmospheric concentration of 5 ng/m^3 (about 3×10^{-11} times the saturation concentration at 20 C, p. 4-8). Hence, we infer a net transfer to the atmosphere across the ocean surface.

No precise figures are available for rates of releases to the ocean. Production losses and disposal into sewers might account for as much as 10 percent of production, but much of this should evaporate before reaching the ocean (p. 4-00). Assuming that 3 to 4 percent of total production enters the oceans, this would represent 3×10^4 tons per year, mostly released into the North Atlantic. If the mean concentration of 0.5 ng/l in the ocean surface layer (Table 4-12) can be extrapolated to the upper 40 m of the Northern Hemisphere oceans, we estimate a total load of approximately 3×10^3 tons. Comparing these figures, we obtain a mean residence time of about a month, which is reasonable if evaporation rates are limited by mixing and diffusion in the oceanic mixed layer. The time scale for degradation in the ocean is of the order of 1 year (Table 4-16), so that evaporation appears to be a much more important route of loss from the ocean.


Release to Atmosphere through dispersive use
Atmosphere
10^4 tons
R.T. 4 days
photo-degradation
9×10^5 tons/yr
Evaporation 3×10^4 tons/yr
Discharge into oceans
3×10^4 tons/yr
Ocean
3×10^3 tons
R.T. 1 month
hydrolysis
3×10^3 tons/yr

According to this preliminary model, Per in the oceans is derived primarily from direct discharge (river transport, ocean disposal, and sewers). If this assumption is correct, concentrations should be highest near populated coasts and decrease progressively down current from them, with a half-life for removal by evaporation of the order of one month: this would lead to spatial gradients with a length scale of some hundreds or thousands of kilometers. Concentrations in the North Atlantic should be much higher than those in the North Pacific.

There are some difficulties in extrapolating this model to other chemicals in the LMCH's group. The relatively high levels of trichloroethylene reported from ocean surface waters (Table 4-12) could be explained if a correspondingly important water route of discharge could be found. The contribution from EDC-tars and other industrial dumping (Table 4-10 and 4-13) appears too small to explain the calculated load of roughly 4 x 10^4 tons. On the other hand, the relatively high levels of trichloroethylene and the low levels of 1,1,1-TCE reported in the atmosphere (Table 4-11) (Murray and Riley 1973) conflict with the reported low reactivity of the latter (Figure 4-6) and high reactivity of the former (Figure 4-5). Both the measurements of concentration and the relevance of the experimental conditions used in the measurements of reactivity need further confirmation. It would also be desirable to measure the vertical distribution of these chemicals in the atmosphere in order to determine the rate at which they are transported upwards into high altitudes.

OVERVIEW

Four low molecular weight chlorinated hydrocarbons (LMCH) were studied: perchloroethylene (Per); 1,2-dichloroethane (EDC); 1,1,1-trichloroethane (1,1,1-TCE); and 1,2-dichloropropane (PDC). All are relatively heavy, volatile liquids with major uses as solvents, degreasing agents, or chemical intermediates. With the exception of 1,2-dichloropropane, annual world production of each is in the range 1 to 9 x 10^5 tons, and is increasing at about 10 percent per year. Substantial quantities of each are released into the atmosphere, with smaller inputs into rivers (Table 4-19).

Experimental studies suggest that these LMCH's should be photolyzed under atmospheric conditions, with half-lives, of the order of hours at high altitudes, but days or longer at sea level. We estimate that half-lives for hydrolysis are of the order of 1 year. A tentative transport model for perchloroethylene suggests the major route of degradation is by photolysis and the residence time in the atmosphere is a few days. The model suggests the main input of perchloroethylene to the ocean is from rivers and sewers and the main route of loss is be evaporation. This model could not be extrapolated to other LMCH's with existing data.

Levels of perchloroethylene, of the order of 10 parts per trillion, have been reported in the atmosphere and the oceans. The other LMCH's studied appear to be present at lower concentrations. Bioaccumulation factors of the order of 10 to 40 have been measured or calculated for fish.

Toxic thresholds for mammals and aquatic organisms are of the order of parts per million, 10^6 or more times the known levels in the environment. There is very little information on sublethal effects, synergisms, antagonisms, or additive effects on marine organisms.

The uses and atmospheric release of the LMCH's studied do not appear to be a hazard. Ocean dumping and perhaps also disposal into rivers of these and other LMCH's and the waste products from their production appear to be of greater concern.

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AROMATIC HYDROCARBONS

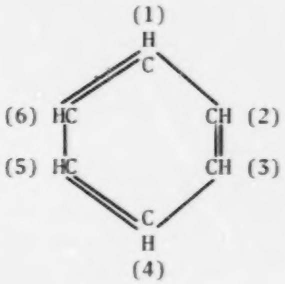
Basic Chemical Properties and Uses

Benzene

Benzene (C_6H_6) is a colorless, volatile, and flammable liquid which is miscible with most organic solvents, particularly alcohols and ether. Water solubility of benzene is 1780 ppm, one of the highest for hydrocarbon substances (McAuliffe 1963, 1966). Benzene forms a two-phase azeotropic mixture with water that boils at 69.25 C. Other physical properties include:

Freezing point:	5.506 C
Boiling point:	80.103 C
Density (20 C):	0.87903
Flash point (closed cup):	-11.1 C
Ignition temperature:	538 C
Explosive limits with air:	1.5 to 8 percent by volume

The chemical stability of benzene is the result of alternating unsaturated bonds that create a stable resonating ring:



Benzene ordinarily undergoes substitution of individual hydrogen atoms, rather than addition reactions.

Common commerical substituted products include: chlorobenzene (ØCl), phenol (ØOH), nitrobenzene (Ø$\mathrm{NO_2}$), aniline (Ø$\mathrm{NH_2}$), ethylbenzene (Ø$\mathrm{CH_2CH_3}$), cumene (Ø$\mathrm{CH_2(CH_3)_2}$), and benzene sulfonic acid (Ø$\mathrm{SO_3H}$). Addition reactions do occur. The predominant substitution compounds, such as $\mathrm{Cl_2}$, $\mathrm{HNO_3}$, $\mathrm{H_2SO_4}$, are electron-seeking or oxidizing agents. Generally these electrophilic agents are not powerful enough to decompose benzene into water and carbon dioxide, because of the chemical stability of the aromatic ring.

Benzene serves as the basic substrate of numerous chemical intermediates and end-products, such as ethylbenzene, aniline, phenol, and cyclohexane which are used in the production of various petrochemical and plastic products (Table 4-20). Exclusive of use as a fuel component, 3.8×10^6 tons of benzene were used in the synthesis of other chemicals.

Toluene

Toluene is a methyl ($\mathrm{-CH_3}$) substituted benzene. Like benzene, it is a colorless, volatile, and flammable liquid. It is sold under the chemical name tolunol. Toluene is miscible with alcohol, acetone, ethyl ether, and carbon disulfide. Its water solubility is 515 to 540 ppm (McAuliffe 1963, 1966), and the solubility of water in toluene is 0.006 mole percent at 10 C. Its physical properties include:

Freezing point:	-94.991 C
Boiling point:	110.625 C
Density (20 C):	0.86694
Surface tension (20 C):	28.53 dynes/cm
Refractive index:	1.49693
Specific heat (20 C):	0.4041
Flash point (closed cup):	4.44 C
Ignition temperature:	552 C
Explosive limits in air:	1.27 to 7 percent
Dipole moment ($\times 10^{18}$):	0.36

TABLE 4-20

Consumption of Benzene For Chemicals (1971)

Compound	Consumption (10^3 Tons)	Per Cent Total Consumption
Ethylbenzene	1,700	44.2
Styrene (polymers, including styrene-butadiene rubber)		
Acetophenone (perfumes, pharmaceuticals, dyes)		
Solvent		
Phenol	730	19.2
Polymers (phenol-formaldehyde; epoxy; polycarbamate)		
Alkyl phenols (lube additives; surfactants)		
Medicinals (salicylic acid), preservatives, herbacides		
Cyclohexane	600	15.6
Cyclohexanol, cyclohexanone, adipic acid, nylon, plasticizers		
Nitrocyclohexane, cyclohexanone oxime, caprolactam, Nylon 6		
Maleic Anhydride	150	3.9
Malic acid (food additive); Malathion (insecticide)		
Maleic hydroxide; textile chemicals; alkyd resins		
Detergent Alkylate	150	3.9
Aniline (via nitrobenzene)	130	3.6
Rubber antioxidants; sulfa drugs		
Diisocyanates, polyurethanes		
Hydroquinone (photographic developer)		
Dichlorobenzenes	40	1.1
Heat-transfer fluid; solvent		
Pesticide; deodorant; dyes		
DDT (Dichlorodiethyl triphenyl methane)	20	0.5
Miscellaneous Nonfuel Uses	310	8.0
Resorcinol (rubber additive, dyes)		
Diphenyl, PCB (heat-transfer fluids)		
Benzene hexachloride (insecticide)		
Total	3,830	

Source: Stanford Research Institute 1972. (Data conversion factor of 7.35 pounds/gallons used.)

Toluene undergoes substitution of hydrogen, either on the aliphatic side-group ($-CH_3$) or on the aromatic ring ($-C_6H_5$). As with benzene, toluene is capable of giving either monosubstituted or multisubstituted products.

Approximately two-thirds of toluene production is converted into benzene by hydrodealkylation. Representative chemical products from toluene are shown in Table 4-21, along with the consumption levels for the primary intermediates.

The major dispersive uses of toluene are as a solvent and as a constituent of motor and aviation gasoline. Toluene solvents for paints, inks, rubber, and adhesives constitute 13 percent of the total demand. Toluene use as a component of motor and aviation fuels in 1966 was estimated to be 7.5×10^4 tons, and this use has probably grown substantially. The trend toward unleaded fuel, with aromatic enrichment needed to preserve a high octane rating, may require more toluene use in fuels.

Production and Consumption

Coal Sources

"Light oil" containing benzene and toluene is obtained from high-temperature carbonization of bituminous coal in coke ovens. Hot gases are cooled and scrubbed with "wash oil" and the aromatic components are then redistilled from the wash oil. Each ton of coal carbonized to coke yields approximately 8 liters of benzene and 2 liters of toluene.

The sixteen major coke-oven operators in the United States had a 1972 benzene production capacity of 3.5×10^5 tons/year. Net toluene production from coal in 1970 amounted to 5.6×10^4 tons/year. These major U.S. plants (Table 4-22) and seven other coke producers obtain light oil from about 6,000 serviceable coke ovens. Some toluene occurring in the light oil is hydrodealkylated to benzene in the light oil refinery; this is tabulated as benzene production. Production sites using coal are almost exclusively in the eastern United States, although Texas and Colorado have some small coal-related enterprises (Figure 4-10). Major coal deposits and their proximity to associated coke markets (particularly the steel industry) in Alabama, Pennsylvania, and Ohio are responsible for situating the majority of the plants for coal-derived benzene and toluene in these inland states. Benzene and toluene produced from coal products have declined steadily since the mid-1950's (Figures 4-11, 4-12).

TABLE 4-21

Consumptive Uses of Toluene (1966)

Product	Consumption (10^3 Metric Tons)	Percent Total Consumption
Benzene	1,100	67.8
Solvents	210	13.2
Toluene diisocyanate Polyurethane plastics	55	3.4
Nitrotoluenes TNT and other explosive forms Dyes	52	3.2
Phenol Phenolic resins	24	1.5
Benzyl chloride Perfumes, flavors, dyes, pharmaceuticals	24	1.5
Benzoic acid Food preservatives, plasticizers, perfumes, dye carriers	7	0.4
Toluene sulfonates Germicides, surfactants	6	0.3
Miscellaneous chemical uses Dyes, flavors, alkyd resins, medicinals	65	4.1
Motor Fuel	57	3.5
Aviation Fuel	18	1.1
Total	1,618	100.0

Source: Stanford Research Institute 1967.

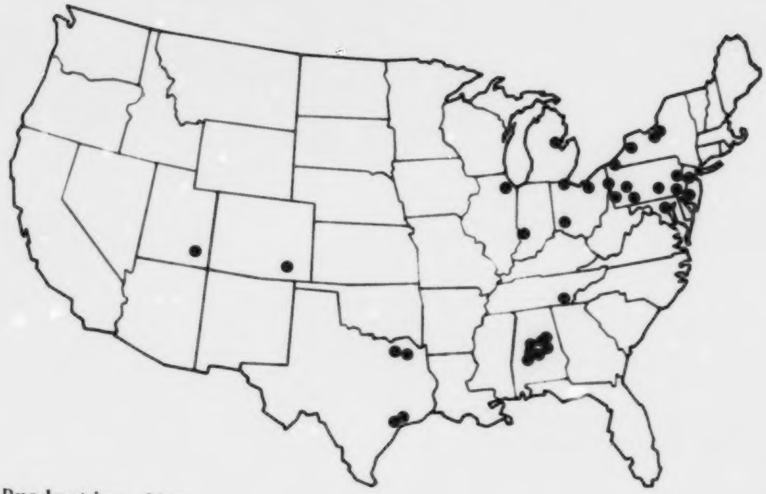
TABLE 4-22

Major Coke-Oven Operators Producing Benzene and Toluene from Coal, January 1, 1972

Company and Location	Benzene Capacity (tons x 10^3 yr.)	Number of Coke Ovens Producing Aromatics
Armco Steel Corporation		
Middletown, Ohio	8	76
Houston, Texas	3	62
Bethlehem Steel Corporation		
Bethlehem, Pennsylvania	19	447
Lackawanna, New York	25	--[1]
Sparrows Point, Maryland	50	757
CF&I Steel Corporation		
Pueblo, Colorado	10	206
Interlake, Inc.		
Toledo, Ohio	6	151
Ling-Temco-Vought (Jones & Laughlin Steel)		
Aliquippa, Pennsylvania	33	271
The Mead Corporation (Woodward-Chattanooga)		
Chattanooga, Tennessee	1	44
Woodward, Alabama	5	256
Northwest Industries, Inc. (Lone Star Steel)		
Lone Star, Texas	5	78
Republic Steel Corporation		
Cleveland, Ohio	22	254
Gadsden, Alabama	4	195
Youngstown, Ohio	12	231
U.S. Steel Corporation		
Clairton, Pennsylvania	134	1,375
Geneva, Utah	13	252
Ovens at other sites	--[1]	1,083
Totals	350	5,738

[1] Data not available in this study.

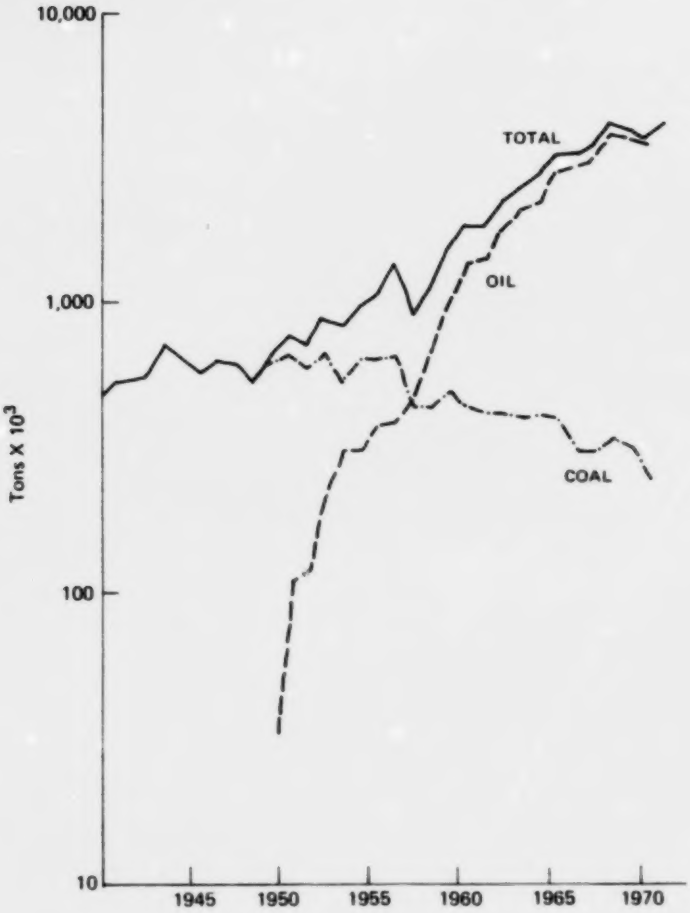
Source: Stanford Research Institute.



Production Sites	
Pennsylvania	7
Alabama	6
Ohio	4
Texas	4
New York	3
New Jersey	2
Utah	1
Colorado	1
Tennessee	1
Indiana	1
Illinois	1
Maryland	1
Michigan	1

FIGURE 4-10

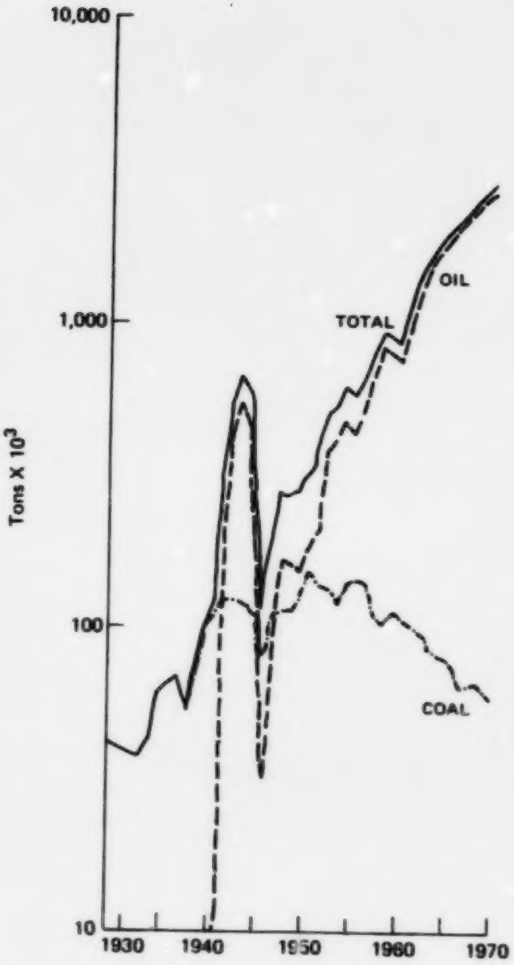
Geographical Distribution of Coal-derived Benzene and Toluene Production Facilities (Includes Coke Oven Plants and Light Oil Distillers)



Source: Stanford Research Institute 1972, U.S. Tariff Commission 1970-1972.

FIGURE 4-11

U.S. Benzene Production from Oil and Coal 1940-1972



Source: Stanford Research Institute 1967, U.S. Tariff Commission 1966-1972.

FIGURE 4-12

U.S. Toluene Production from Oil and Coal 1930-1970

Petroleum Sources

Although the natural benzene and toluene content of most crude oils is fairly low, aromatics from petroleum dominate the total production because of the tremendous volume of oil processed annually and the formation of aromatics during refining. The major quantity of aromatics is obtained from catalytic cracking and catalytic reforming, which yield distillate fractions containing up to 45 percent aromatics by volume. In catalytic cracking and reforming, nonaromatic compounds (cyclopentanes, cyclohexanes, and also paraffins) are converted to aromatics.

The actual amount of toluene obtained during olefin manufacture is determined by the raw materials used and the physical conditions during cracking, so no accurate relationship to total ethylene production can be determined. Generally, with naphtha as a feed for olefin production, 50 to 70 pounds of aromatics are produced for every 100 pounds of ethylene, including up to 50 pounds of benzene and up to 12 pounds of toluene.

In 1971, fifty-six domestic refineries and two in Puerto Rico utilized petroleum products to produce benzene and toluene (Tables 4-23, 4-24 and Figure 4-13). Total plant capacity exceeds current production by approximately one-third.

Aromatic production by the petrochemical industry is located predominantly along the western Gulf of Mexico. Texas (29 facilities) and Louisiana (7 producers) account for two-thirds of total United States facilities and an equivalent fraction of total production capacity (Table 4-23). The geographical distribution of the domestic benzene and toluene producers from petroleum shows coastal concentrations, especially along Texas estuaries, the lower Mississippi River in Louisiana, Delaware Bay, Puerto Rico and the California Coast near Long Beach (Figure 4-13).

Imports and Exports

Import and export data are an indicator of the marine shipment of benzene and toluene, and thus of the potential for losses to the ocean through spillage and tanker

TABLE 4-23

Petroleum-Derived Benzene and Toluene Production Capacity by State

State	Number of Plants	Benzene Capacity 10^3 tons/yr.	Toluene Capacity 10^3 tons/yr.
Texas	29	2,200	1,500
Puerto Rico	2	900	360
Louisiana	7	780	390
Illinois	2	230	79
Kentucky	2	200	66
California	3	170	160
Pennsylvnia	3	160	180
Michigan	3	120	72
New Jersey	1	120	--
New York	1	--	46
Kansas	2	40	39
Oklahoma	2	40	98
Mississippi	1	--	--
Total (11 States)	58	4,960	2,990

Source: Stanford Research Instutute January, 1972.

TABLE 4-24

Plants Producing Benzene and Toluene from Petroleum (includes plants using purchased coal light oils)

		Benzene Capacity	Process
Allied Chemical Corp.	Winnie TX	16.71	A
American Petrofina, Inc.	Big Spring TX	100.23	A,B
Ashland Oil, Inc.	Ashland KY	200.46	A,E
	Catlettsburg KY	--	--
Atlantic Richfield Co.	Buffalo NY	--	--
	Houston TX	145.80	A,C
	Nederland TX	--	--
	Wilmington CA	53.50	A
Charter International Oil Co.	Houston TX	26.70	A
Cities Service Co., Inc.	Lake Charles LA	83.65	A
Coastal States Gas Producing Co.	Corpus Christi TX	33.41	A
Continental Oil Co.	Lake Charles LA	--	--
	Ponca City OK	--	--
Commonwealth Oil Refining Co.	Penuelas PR	535.00	A,B
Crown Central Petroleum Corp.	Houston TX	16.71	A
Dow Chemical Company	Bay City MI	100.23	B,E
	Freeport TX	133.70	B
Gulf Oil Company	Alliance LA	234.00	A,B
	Philadelphia PA	110.02	A,B
	Port Arthur TX	127.00	A,D
Hess Oil & Chemical Corp.	Corpus Christi TX	--	--

(continued)

TABLE 4-24 (continued)

Leonard Refineries, Inc.	Mt. Pleasant MI	--	--
Marathon Oil Company	Detroit MI	20.02	A
	Texas City TX	20.02	A
	Beaumont TX	--	--
Mobil Oil Corp.	Beaumont TX	200.46	A,D
Monsanto Company	Alvin TX	250.30	B,D
	Texas City TX	--	--
Pennzoil United Inc.	Shreveport LA	40.10	D
Phillips Petroleum Co.	Sweeny TX	73.60	A
	Guayama PR	368.00	A,B
Pontiac Refining Co.	Corpus Christi TX	--	--
Shell Oil Company	Deer Park TX	217.00	D
	Odessa TX	16.71	A
	Wilmington CA	66.82	A,E
	Wood River IL	133.64	A,E
Signal Oil & Gas Co.	Houston TX	--	--
Sinclair Oil Corp	Houston TX	--	--
Skelly Oil Company	El Dorado KA	40.10	E
South Hampton Company	Silsbee TX	--	--
Southwestern Oil & Refining Co.	Corpus Christi TX	26.70	A
Standard Oil of CA	El Segundo CA	50.11	A
Standard Oil of IND	Texas City TX	284.00	A
Standard Oil of KY	Pascagoula MISS	--	--
Standard Oil of NJ (Enjoy Chemical)	Baton Rouge LA	200.46	A,D
	Baytown TX	--	--
Sun Oil Company	Marcus Hook PA	50.11	A
	Corpus Christi TX	50.11	A,E
	Tulsa OK	40.10	A

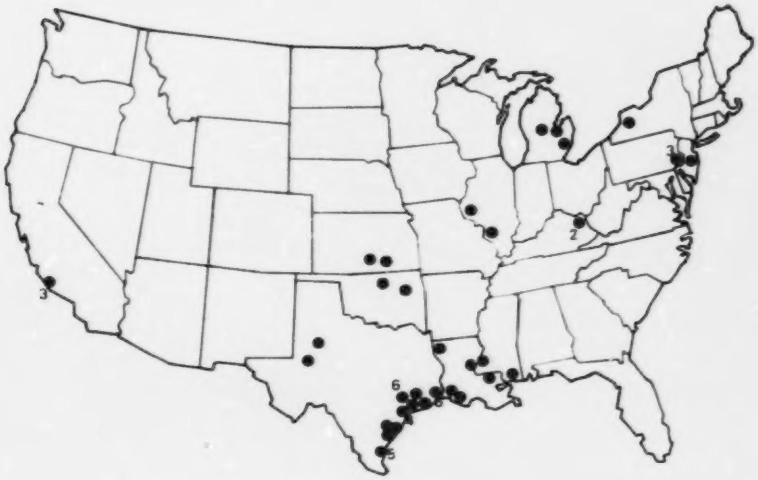
(continued)

TABLE 4-24 (continued)

Tenneco, Inc.	Chalmette LA	50.11	A,E
Texaco, Inc.	Port Arthur TX	150.20	A
	Westville NJ	116.90	A
Union Carbide Corp.	Taft LA	167.05	D
	Seadrift TX	--	--
Union Oil Co. of CA	Lemont IL	100.23	A,E
	Nederland TX	--	--
Union Pacific Corp.	Corpus Christi TX	30.30	A
Vickers Refining Co. Inc.	Potwin KA	--	--

Process Code:

A - catalytic reformate
B - toluene dealkylation
C - toluene disproportionation
D - isolation from pyrolysis gasoline
E - frationation of purchased light oils



Production Sites

	Benzene	Toluene	Total
Texas	20	23	29
Louisiana	6	5	7
California	3	3	3
Pennsylvania	2	3	3
Illinois	2	2	2
Michigan	2	2	3
Kentucky	1	1	2
New Jersey	1	–	1
Kansas	1	2	2
Oklahoma	1	2	2
Mississippi	–	1	1
New York	–	1	1

Area of Concentration

Galveston Bay, Neches-Sabine River
Corpus Christi Bay
Lower Mississippi River, Lake Charles
Long Beach Area
Delaware River
Upper Mississippi

FIGURE 4-13

Geographical Distribution of U.S. Petroleum-Derived Benzene and Toluene Production Facilities cleaning. The number of foreign production sites (Table 4-26) suggests the extent of worldwide transportation and use.

Benzene Imports of benzene exceeded exports by the United States in 1971, reversing the production expansion and trend toward greater exports during the 1960's (Table 4-25). Quantities of imported benzene approximate the current domestic benzene production from coal-derived sources. Mexico, Canada, and Japan supply over 75 percent of current imports, with Caribbean islands (the Netherlands Antilles and Trinidad) furnishing lesser quantities. Japan furnished more benzene than all European production facilities combined.

European consumers, such as the Netherlands, United Kingdom, and Italy purchase the majority of United States benzene exports. Smaller quantities are also shipped to Canada, Brazil, and Australia. As domestic consumption increases and more imports are required to compensate for the difference between production and consumption, exports of pure benzene should decrease. However, benzene-derived products are expected to constitute a larger share of future United States chemical exports (Stanford Research Institute 1972).

Toluene Toluene imports to the United States during the past decade increased from 1.64×10^3 tons in 1962 to 4.87×10^5 tons in 1972. Imports currently amount to 20 percent of total United States production. The demand for explosives and aviation gasoline during the Viet Nam War may have been responsible for increased toluene demand. Imports of toluene rose faster than imports of benzene, suggesting increased use of toluene as a chemical intermediate rather for dealkylation to benzene.

Ninety-one companies were known to be producing toluene outside the United States in 1966, excluding the major Soviet bloc countries for which data were not available (Table 4-26) (Stanford Research Institute 1967). Japan, Italy, Canada, and the Netherlands Antilles ship the greatest quantities of toluene to this country.

In 1972, 80×10^3 tons of toluene were exported by the United States, continuing a decline from 198×10^3 tons in 1963 (Table 4-27). The United States currently exports toluene to more than eighteen countries,

TABLE 4-25

U.S. Imports and Exports of Benzene and Toluene
(1952 to 1972)

	Annual U.S. Imports (10^3)		Annual U.S. Exports (10^3)	
Year	Benzene	Toluene	Benzene	Toluene
1972	317.6	487.2	93.2	80.0
1971	253.2	367.0	142.3	47.5
1970	175.0	305.0	223.7	67.6
1969	217.0	162.4	307.0	103.6
1968	110.0	105.1	278.0	118.17
1967	85.3	100.8	341.5	80.6
1966	76.6	95.50	308.0	166.95
1965	82.3	44.28	151.5	153.83
1964	51.2	16.10	292.0	186.63
1963	43.8	10.82	216.1	198.44
1962	71.0	1.64	138.0	182.37
1961	62.2	5.25	155.3	138.74
1960	126.2	9.84	79.0	167.28
1959	182.0	4.59	24.4	102.99
1958	147.5	2.30	38.4	84.30
1957	176.00	2.62	9.0	80.36
1956	220.3	0.0	9.0	28.54
1955	102.0	0.0	8.4	38.38
1954	39.8	0.0	19.7	69.54
1953	65.6	0.0	4.0	12.10
1952	137.5	0.33	0.67	0.0

Source: Stanford Research Institute 1967, U.S. Bureau of the Census 1967-1972a, 1967-1972b.

TABLE 4-26

U.S. Imports of Benzene and Toluene by Country (1972)

	Toluene			Benzene	
Country	Number of Producing Companies	Quantity Imported (10^3 tons)	Percentage of total imports	Quantity Imported (10^3 tons)	Percentage of total imports
Canada	5	59	12	44	25.0
Mexico	1	6	1.1	41	23.7
San Salvador	*	7	1.4	--	--
Panama	*	2	0.4	--	--
Trinidad	1	34	6.9	8	4.3
Netherland Antilles		51	10.4	8	4.7
Colombia	1	18	3.8	--	--
Venezuela	1	4	0.7	--	--
United Kingdom	15	4	0.7	--	--
Netherlands	2	25	5.1	6	3.6
Belgium	9	27	5.7	--	--
USSR	*	2	0.5	--	--

(continued)

TABLE 4-26 (continued)

Spain	1	8	1.7	--	--
Italy	11	86	17.7	--	--
Yugoslavia	*	22	4.6	--	--
Romania	1	5	1.1	2	1.1
Japan	16	127	26.1	59	33.7
France	6	--	--	2	1.2
Argentina	3	--	--	5	2.7
Other Countries	18*	--	--	--	--
Totals	91*	487	100	175	100.0

*Complete information on production sites not available

Source: U.S. Bureau of the Census 1967 to 1972a.

TABLE 4-27

U.S. Exports of Benzene and Toluene by Country (1972)

Country	Toluene Quantity Exported (10^3 tons)	 Percentage of total exports	Benzene Quantity Exported (10^3 tons)	 Percentage of total exports
Canada	0.9	1.1	17.3	7.8
Mexico	0.2	0.3	--	--
Guatemala	0.6	0.8	--	--
Nicaragua	1.0	1.2	--	--
Costa Rica	0.6	0.8	--	--
Venezuela	4.3	5.4	--	--
Peru	0.6	0.7	--	--
Chile	2.0	2.5	--	--
Brazil	35.5	44.4	5.2	2.8
Argentina	0.2	0.2	--	--
United Kingdom	--	--	55.2	24.7
Netherlands	17.0	21.2	130.6	58.5

(continued)

TABLE 4-27 (continued)

Italy	--	--	12.6	5.6
Pakistan	1.9	2.4	--	--
Thailand	4.1	5.2	--	--
South Viet Nam	0.8	1.0	--	--
Malaysia	3.5	4.4	--	--
Phillipines	3.9	4.9	--	--
Hong Kong	2.2	2.7	--	--
Australia	0.2	0.3	1.0	0.4
Other Countries	0.4	0.5	1.5	0.7
Totals	79.9	100	223.4	100

particularly in the Western Hemisphere and in Southeast Asia. The Netherlands is the only European country to receive United States-produced toluene, amounting to one-fifth of total exported quantities. Brazil imports 44 percent of the total United States export supply or 35.5 x 10^3 tons, while all other countries import less than 5 x 10^3 tons each.

Biological Effects

Investigations of the biological effects of water-soluble extracts of crude oil and associated refined products have attempted to assay the entire light hydrocarbon fraction which includes the more soluble aromatic hydrocarbons. Numerous implied similarities can be drawn from benzene and toluene effects on aquatic organisms because they are both present in crude oils, comprise a large percent of refined products, and are relatively water-soluble. The differences between aromatic toxicity and overall petroleum toxicity in the aquatic environment are largely undefined.

Toxicity to Aquatic Organisms

Due to the close chemical relationship between benzene and toluene, toxicity investigations with one compound usually include the other. This association reflects the combined presence of both of these aromatic hydrocarbons in coal-derived light oils and crude petroleum and their simultaneous release into the environment via waste effluents or dispersive uses (e.g., gasoline consumption).

Investigations of benzene and toluene toxicity to aquatic organisms have generally evolved from analysis of the toxic components in coke production by-products and petrochemical refinery effluents (Shelford 1917, Turnbull *et al.* 1954, Pickering and Henderson 1966) to a concern about the aromatic component in crude petroleum spills and other oil discharges (Kittredge 1971, Zitko and Tibbo 1971, Brocksen and Bailey 1973, Kauss *et al.* 1973). Improvements in treatment capability at stationary sources such as refineries, petrochemical plants, and coke production plants (U.S. Environmental Protection Agency 1972) may be reducing the quantities of aromatics that are released to rivers and estuaries.

Plants North *et al.* (1959) examined the effect of benzene and toluene on the giant kelp, *Macrocystis pyrifera*. They observed no effect on photosynthetic activity over a 96-hour period of exposure at 10 ppm benzene, whereas toluene greatly reduced photosynthesis with the same exposure. Currier (1951) examined the herbicidal properties of benzene and associated aromatics and demonstrated that the toxicity of toluene exceeded that of benzene. His work with partition coefficients (water to paraffin oil) of benzene, toluene, xylene, and trimethylbenzene demonstrated an inverse relationship between toxicity and compound solubility. He concluded that cellular penetration was facilitated by increasing the number of methyl groups on the benzene ring. This indicates that the expected benzene toxicity to plants is less than the toxicity for alkylated benzene.

Invertebrates Kittredge (1971) observed definite chemoreception abnormalities in marine crabs caused by sublethal concentrations of benzene. While primarily looking at the effects of the water-soluble component of crude oil on marine crustaceans, he observed that feeding behavior in the Lined Shore Crab (*Pachygrapsus crassipes*) was inhibited by pure benzene or naphthalene, as well as by an aqueous extract of crude petroleum containing these aromatics. However, the concentrations initiating this disruption were not given. The inhibition of feeding by benzene also tended to be more transient than that observed for the more complex crude petroleum extracts.

Bringmann and Kühn (1959) reported threshold toxicities of 60 ppm toluene for *Daphnia*. This is significantly lower than the minimum toxicity levels of 120 ppm for *Scenedesmus* and 200 ppm for *Escherichia coli*.

Lee *et al.* (1972) found ^{14}C-labelled toluene was not metabolized by the mussel *Mytilus edulis*, and was released from its tissues after transfer to fresh seawater. Toluene in concentrations up to 1 ppm did not have a lethal effect on *Mytilus*, but an inhibition of filtering ability may have occurred due to chemoreceptor detection of the aromatic hydrocarbon and subsequent alteration of the filtering rate. Paraffin-type hydrocarbons are less toxic to the mussel than the aromatics and were taken up to a much greater extent (milligram compared to microgram quantities). This may be significant in determining sublethal toxicity for aquatic invertebrates.

Vertebrates The acute toxicity of benzene and toluene on vertebrates has been investigated by several authors (Table 4-28).

Shelford (1917) evaluated the toxicity of waste by-products from the destructive distillation of coal. The sunfish used by Shelford, *Lepomis humilis*, died in concentrations of 35 to 37 ppm benzene and 61 to 65 ppm toluene within one hour. Behavioral abnormalities, such as erratic movement, leaping out of the tank, and intoxication, often preceded death.

Turnbull *et al.* (1954) reported TLm (levels lethal to 50 percent of the test population within the specified time) values of 20 ppm for benzene at 24 to 48 hours and calculated that 6 ppm was a safe concentration based on acute toxicity. Behavioral observations indicated intermittent violent movement and distress when benzene concentrations were between 20 and 34 ppm.

Acute toxicity of benzene to several freshwater fish was investigated by Pickering and Henderson (1966). Fathead minnows (*Pimephales promelas*) exhibited slightly more resistance to benzene toxicity in hard water. However, none of the other fish species were tested for variability in water hardness. A TLm of 22.5 ppm for all exposure intervals to benzene was reported for bluegills (*Lepomis macrochirus*). Twenty-four hour TLm values of 34.4 ppm and 36.6 ppm, respectively, for goldfish (*Carassius auratus*) and guppies (*Lebistes reticulatus*) were reported for benzene, and the TLm (24 hour) for fathead minnows was 35.5 ppm for soft water and 34.4 ppm for hard water.

Pickering and Henderson (1966) also tested the identical species for sensitivity to toluene. Bluegills were most susceptible to toluene poisoning (24 ppm), with fathead minnows, goldfish, and guppies showing almost equal toxic limits (56 to 62 ppm). Soft water increased the toxicity of toluene to fathead minnows by almost 10 ppm. Slight differences occurred in TLm values between 24- and 96-hour test exposures for fathead minnows.

Measurements of the respiratory stress exhibited by chinook salmon (*Oncorhynchus tsawytscha*) and striped bass (*Morone saxatilis*) when exposed to sublethal benzene concentrations in freshwater were investigated by Brocksen

TABLE 4-28

Reported Benzene and Toluene Toxicity to Aquatic Animals

Acute Toxicity Effects	Concentration (ppm) resulting in death of all organisms within		Benzene (Toulene)* Reported TL_m Values (ppm)			Reference
	2 Hours	24 Hours	24 Hours	48 Hours	96 Hours	
Organism:						
Pimphales promelas (fathead minnow)	--	--	35.56 (46.31)	35.08 (46.31)	33.47 (34.27)	3
Lepomis macrochirus (bluegill)	--	--	22.49 (24.00)	22.49 (24.0)	22.49 (24.0)	3
Carassius auritus (goldfish)	--	--	34.42 (57.68)	34.42 (57.68)	34.42 (57.68)	3
Lebistes reticulatus (guppies)	--	--	36.60 (62.81)	35.60 (60.95)	36.60 (59.30)	3
Lepomis machrochirus (bluegill)	60	34	--	--	--	2
Lepomis humilis (orange-spotted sunfish)	35-37 (61-65)	--	--	--	--	1

*Toxic levels of toluene are given in parentheses

(continued)

TABLE 4-28 (continued)

Sublethal Toxicity Effects	Concentration (ppm) at which Sublethal Effects Noted	Reported Effects	Reference
Organism:			
Oncorhynchus tshawytscha (chinook salmon)	5	Increased respiration rate	5
Morone saxatilis (striped bass)	5	Increased respiration rate	5
Pachygrapsus crassipes (lined shore crab)	-	Decreased chemotaxic response to food or sex hormones	4

Sources:
1 Shelford 1917
2 Turnbull 1954
3 Pickering and Henderson 1966
4 Kittredge 1971
5 Brocksen and Bailey 1973

and Bailey (1973). Respiration rates of juvenile chinook salmon increased when exposed to 6 ppm benzene and were 115 percent above normal levels after 48 hours of exposure to 5 and 10 ppm. A mean respiration increase of 50 percent at 24 hours was noted for striped bass at 5 ppm, but respiration increased only 15 percent over an entire 96-hour exposure at 10 ppm. A narcosis and associated depression of respiration to below normal levels was evident among striped bass exposed for 48 hours at 5 ppm and 24 hours at 10 ppm, but recovery proceeded fairly rapidly. A doubling of current velocities in the respirometer produced more rapid recovery from the narcotic effect by increased flushing of benzene from the gill filaments and increased oxygen availability.

The probable physiological pathways followed by benzene in fish were described by Brocksen and Bailey (1973). Benzene is absorbed across the gill surface into the blood where it becomes attached to erythrocytes and lipoproteins for transport to lipid-rich tissues. While metabolism to phenol is accomplished by the liver, kidney, and various body tissues, a portion of the benzene is excreted unchanged through the gills. Benzene appears to follow the same biochemical pathway as in the hydroxylation of sterols and pre-oxidation of lipids. A buildup of benzene due to overloading the hydroxylation mechanisms for conversion to phenol or competition with lipid oxidation results in deposition within the lipid-rich nervous system and narcosis.

Brocksen and Bailey (1973) postulated that the HMP (hexose monophosphate) shunt in a fish with low lipid content does not supply the $NADH_2$ needed for enzymatic detoxification of benzene, and that the hydrocarbon is catabolized directly to carbon dioxide and water. This action results in slowed detoxification, increased accumulation of benzene, and a longer period of narcosis. Since the chinook salmon were shown to possess fewer lipids in the total body fat (11 percent) than striped bass (21 percent), this mechanism may be a factor in the different respiratory responses observed for the two species. In addition, an experimental variation (smaller average size for the test salmon) may have resulted in greater benzene assimilation and excretion problems for them.

Implied Effects of Aromatic Hydrocarbons We assume a relationship between observed toxicity of petroleum extracts and potential effects of aromatic hydrocarbons. Wasik and Brown (1973) found benzene and toluene were the most prevalent hydrocarbons in the seawater extracts of petroleum. Gilfillan (1973) found small quantities (1 ppm) of oil extracts reduced feeding rate, slowed assimilation of filtered food, and increased respiration in two species of mussel (*Mytilus edulis* and *Modiolus demissus*). Simultaneous metabolic stresses, particularly osmoregulatory requirements in various salinities, were shown to intensify the toxic effects of oil. These results may indicate other sublethal effects which could affect the resident fauna and reduce their ability to withstand other stresses.

Water-soluble extracts of No. 2 distillate fuel oil, No. 6 fuel oil, and outboard motor oil were tested on *Chlorella*, *Chlamydomonas*, *Skeletonema*, and *Phaeodactylum* (Nuzzi 1973). No. 2 fuel oil was more toxic than No. 6 fuel oil or outboard motor oil (heavy oils low in aromatics). Low molecular weight aromatics, or possibly the naphthalene component, may have been the causative agent, although this was not determined. The diatoms, which have the largest lipid contents among the phytoplankton species tested, were most sensitive to the hydrocarbons. Partitioning of aromatic hydrocarbons into the lipid component of diatoms may have enhanced the phytotoxicity.

The heavier, more insoluble, oils, have only small aromatic components and their overall toxicity appears negligible (Nuzzi 1973). For example, a spill of No. 6 fuel oil into Galveston Bay in 1973 introduced 2.5 ppb benzene into subsurface waters (8 feet depth) in the vicinity of the spill (C. B. Koons 1973, pers. comm.). This aromatic content reflects the nature of the oil product spilled, but the physical characteristics of estuarine systems may have helped to reduce observed benzene levels. Lighter petroleum products with higher aromatic contents would be expected to introduce larger quantities of aromatics after spillage.

Zitko and Tibbo (1971) showed that spilled intermediate oil from coke production caused a fish kill of herring (*Clupea harengus*) in North Sydney Harbor, Nova Scotia. Histological examination showed that oil, which contained a considerable proportion of aromatics, was taken up through the skin of the fish. Tissue concentrations of oil in various parts of the herring were 17.5 mg/g (skin), 5.2 mg/g (muscle), and 9.2 mg/g (intestine).

"Water-dispersible fractions," presumably including the soluble aromatics, were the suspect toxic agents after spillage from Shell Platform B, South Timbalier Bay on the Louisiana Coast (Resources Technology Corp. 1972). Petroleum hydrocarbons were transported downward through the water column (30 meters deep) and deposited in the sediments. Observations indicated hydrocarbon-containing sediments could be readily redispersed into the surrounding water although some sediment residues appeared to be long-lasting. Sediments near the discharging platform contained 4500 ppm hydrocarbons (CCl_4 extractable), while samples taken four miles away contained 100 ppm hydrocarbons.

Sampling of the benthic organisms inhabiting the oil-polluted sediments revealed an inverse relationship between megafaunal counts per square meter and concentrations of sediment hydrocarbons (Resources Technology Corp. 1972). The numbers of benthic organisms also decreased approaching the discharging platform from three different directions, indicating wind-dominated dispersion of the hydrocarbons. The potential for release from the sediments indicates that benthic organisms may be exposed to soluble hydrocarbons after actual spillage ceases.

Biodegradation

Biodegradation of aromatic hydrocarbons occurs in activated sludge treatment systems. Buzzell *et al.* (1968) found that 10 mg/l concentrations of toluene were reduced by 32 percent within 20 days in an aquatic system inoculated with sewage sludge microorganisms. Adapted or acclimated cultures of bacteria can be developed that utilize aromatic hydrocarbons. Activated sludge organisms, acclimated to aniline, degrade benzene at a rate half that of toluene (Malaney 1960). If phenol is used to acclimate the bacterial culture, degradation of benzene is very slow (Chambers *et al.* 1963). Benzene acclimated microorganisms oxidized 500 mg/l benzene by 35 percent and toluene by 48 percent within 196 hours. However, less than 3 percent oxidation of benzene was observed by Bogan and Sawyer (1955) using various BOD and Warburg respirometer techniques with nonaromatic acclimated bacteria.

Soil microorganisms have been isolated which utilize aromatic hydrocarbons, especially toluene. Kapralek (1954) found a pseudomonas-type bacteria from the soil of a petroleum deposit that utilized toluene, but not benzene. *Pseudomonas* and *Achromobacter* from soil can use benzene and toluene as the sole carbon source for growth (Claus and Walker 1964, Gibson and Yeh 1972).

Metabolic pathways for bacterial oxidation of the benzene ring have been identified (Gibson 1972). Microorganisms enzymatically convert benzene to catechol (dihydroxybenzene) before cleaving the ring and ultimately degrading the compound to CO_2 and water (Marr and Stone 1961, O'Connor *et al.* 1964, Gibson *et al.* 1968). Phenol may appear as a metabolite, but the pathway typically produces catechol as the primary intermediate. Toluene appears to follow an analogous enzymatic pathway, with either the methyl group oxidized to form benzoic acid or the ring hydroxylated directly (Gibson 1972) before yielding 3-methylcatechol as the end product. Ortho-cresol may be detected as a nonenzymatically formed metabolite.

Metabolism and Bioaccumulation

Conversion to catechol for benzene and 3-methylcatechol for toluene in rabbit liver (Jerina *et al.* 1968) have been demonstrated. Phenol can result from an alternate pathway, and is generally conjugated with sulfates and glucuronic acid in the blood and excreted in this form by mammalian systems (Porteous and Williams 1949). Copepods cannot metabolize aromatic hydrocarbons (Lee *et al.* 1972).

Brocksen and Bailey (1973) postulated that the lipid content of fish exposed to aromatic hydrocarbons may directly affect the physiological fate of accumulated substances.

The partitioning of benzene and toluene between lipid and water phases can be estimated by partition coefficients between ethanol and water. Data from Dow Chemical USA (1973, unpublished data) and Leo *et al.* (1971) suggest a higher concentration of aromatic hydrocarbons in the lipids of marine animals than in the surrounding water. This bioconcentration is small in comparison to that of persistent chlorinated forms such as DDT and hexachlorobenzene.

Partitioning of aromatic hydrocarbons across the skin and gills in fishes may be responsible for the tainting of fish flesh in waters containing low aromatic concentrations. Investigations of unpalatable fish from the lower Mississippi River have been tentatively correlated with aromatics and other biorefractory substances being discharged in the area (USEPA 1972).

Aromatic Hydrocarbons in the Atmosphere

Detection of Aromatics in the Atmosphere

Gas chromatography is the primary method for determining aromatic hydrocarbons in the atmosphere, and is capable of detecting parts per billion concentrations. Analytical methods for sampling and analyzing aromatic hydrocarbon pollutants (including benzene and toluene) in the atmosphere have been described by Salvadeo *et al.* (1963), Novak *et al.* (1965), Williams (1965), Reid and Halpin (1968), Grob and Grob (1971), and Pilar and Graydon (1973).

Atmospheric Hydrocarbon Sources

Sources of atmospheric hydrocarbons are primarily automobile exhaust (Lonneman *et al.* 1968, Pilar and Graydon 1973), solvent uses (Zeman and Kvasnicka 1966), and production facilities (Masek and Sedlak 1970).

Petrochemical industries in Russia were found to have 6 to 29 mg/m^3 benzene around outside installations (Kapkaev *et al.* 1966). The interior atmosphere of a Maryland chemical reclamation plant contained concentrations of 23 ppm benzene and 11 ppm toluene (Smoyer *et al.* 1971). These atmospheric levels are several orders of magnitude higher than those found for urban environments where automobile exhaust is the major source. The extent of losses from petroleum refining activities and chemical facilities utilizing these aromatic hydrocarbons as intermediates remain to be determined.

Atmospheric Concentrations

Because of the air pollution generated by automobile exhaust in the Los Angeles basin, measurements of aromatic hydrocarbons are rather extensive (Altshuller and Bellar 1963, Lonneman *et al.* 1968, Altshuller *et al.* 1971). The combined concentrations for benzene and toluene over an eight-day period in 1963 for Los Angeles averaged 0.05 ppm. Benzene and toluene comprised over half of the total aromatics fraction, with toluene concentrations slightly higher than benzene (Altshuller and Bellar 1963).

Analysis for aromatic hydrocarbons in the Los Angeles atmosphere in 1966 (Lonneman *et al.* 1968) revealed a 0.11 ppm average for total aromatics. Benzene concentrations averaged 15 ppb by volume, with toluene the most abundant aromatic hydrocarbon (37 ppb average). The average ratio of toluene to benzene was 2.5 in air samples. Since toluene-to-benzene ratios average 1.8 for automobile exhaust emissions, Lonneman *et al.* (1968) suggested that toluene solvent losses to the atmosphere may be significant in explaining the observed difference. Altshuller *et al.* (1971) describe the diurnal composition of atmospheric hydrocarbon pollutants, specifically toluene, in Los Angeles for the fall of 1967. Daily alkylbenzene averages from 5:00 a.m. to 4:00 p.m. were 0.084 ppm for Los Angeles. Toluene occurred in highest concentrations among all aromatics, and averaged 30 ppb in all Los Angeles air samples and one-half that in suburban Azusa. Toluene was noted to contribute to the eye irritation potential of the area air pollution.

Pilar and Graydon (1973) found an atmospheric toluene-to-benzene ratio of 2.3 in Toronto. Average concentrations of benzene (13 ppb) and toluene (30 ppb) are comparable to those reported in previous Los Angeles investigations and correlated well with daily traffic peaks. Samples taken away from the city on an island that lacked vehicular traffic showed aromatic hydrocarbons dispersed downwind from the urban area. It appears that atmospheric transport from urban coastal areas represents a possible mechanism for benzene and toluene introduction to marine environments. Grob and Grob (1971) found a toluene-to-benzene ratio in Zurich of 0.72 to 1. Pilar and Graydon (1973) attributed this variation from reported

North American values to differences in climate, gasoline consumption, and the predominant types of emission source.

Fate in the Atmosphere

Little information is available on the atmospheric behavior of benzene. It appears to be relatively unreactive in atmospheric smog (Altshuller and Bellar 1963). Povov (1971) reported that minimal concentrations of NO_2 were produced when benzene vapors and nitric oxide reacted under ultraviolet irradiation.

When toluene and nitric oxide were reacted under ultraviolet light, toluene produced oxidant, but at a slower rate than other aromatic and olefin hydrocarbons tested, (Altshuller *et al.* 1962). Small amounts of peroxyacetyl nitrate (oxidant) are produced by irradiation of toluene and nitric oxide.

The ultimate fate of aromatic hydrocarbons, especially benzene, injected into the atmosphere is largely unknown, but a slow photochemical process is a reasonable postulation. In general, aromatic hydrocarbons appear to be more resistant to photolytic decomposition by high energy electron irradiation than other hydrocarbons (Hentz and Burton 1951). Because benzene appears to be relatively inactive in smog-producing photochemical reactions and only slightly affected by ozone and ultraviolet radiation, the atmospheric degradation may be quite slow in comparison to other aromatics and aliphatic hydrocarbon pollutants, thus permitting a longer residence time in the atmosphere. Toluene from automobile exhaust emissions and solvent losses appears to degrade with the production of some oxidant and nitrogen dioxide.

Data on particulate sorption by benzene and toluene are not available, although Kapkaev *et al.* (1966) indicated that sorption and desorption of benzene from petrochemical plant buildings did occur. The general mode of transport into oceans is not known.

Aromatics in Marine Waters

Detection

Infrared and ultraviolet spectrometry and a combination of gas chromatography and mass spectrometry have been used for detection of aromatic hydrocarbons (including benzene and toluene). Infrared spectrophotometry has been used to analyze for aliphatic and aromatic petroleum hydrocarbons, phenols, and other refinery wastewater compounds (Rosen and Middleton 1955), and detection limits below 1 ppm have been claimed for some wastewater components (Simard *et al.* 1951). However, the quantification of individual aromatic compounds was not achieved using these methods. Mosecu and Dacin (1971) developed an ultraviolet spectrophotometric technique that could detect benzene down to 0.8 ppm in wastewater samples.

Chromatographic methods appear best for determining the concentration of aromatic hydrocarbons in trace or contaminant quantities. Desbaumes and Imhoff (1972) describe a method for analyzing various aromatic solvents in drinking water and wastewater using a flame ionization gas chromatograph. Gas-liquid chromatography worked well in detecting industrial solvents including benzene and toluene, in domestic wastewater (Lewin *et al.* 1972).

Benzene and toluene have been identified in municipal drinking water and river water(Table 4-29). Kleopfer and Fairless (1972) used flame ionization gas chromatography to detect toluene among the forty organic compounds in Evansville, Indiana municipal drinking water. McAuliffe (1971) found 2.0 ppb benzene and 0.2 ppb toluene in municipal tap water from Louisiana. Polluted drinking water in Prague, Czechoslovakia had a benzene and toluene content of approximately 1 ppb each, determined by gas chromatography-mass spectrometry, and a sample of "pure" drinking water contained an equivalent amount of benzene (Novak *et al.* 1973).

Analysis of lower Mississippi River water by gas chromatography/mass spectrometry techniques revealed the presence of 34 different organic chemicals, including benzene and toluene (U.S. Environmental Protection Agency 1972). No actual concentrations were given, but the compounds persisted in raw and finished municipal drinking water downstream from the suspected discharges.

TABLE 4-29

Aromatic Hydrocarbons Detected in Water Supplies

Substance	River Basin	Location	Type of Sample	Reference
Benzene	Mississippi	U.S. Public Health Service Hospital Carville, Louisiana	Drinking Water	1
	Mississippi	Carrollton Water Plant New Orleans, Louisiana	Drinking Water (Finished)	1
	-	Prague, Czechoslovakia	Drinking Water (pure and polluted samples)	3
	Potomac	Washington, D.C.	Drinking Water	4
Toluene	Ohio	Evansville, Indiana	Drinking Water	2
	Mississippi	U.S. Public Health Service Hospital, Carville, Louisiana	Drinking Water	1
	Mississippi	Carrollton Water Plant New Orleans, Louisiana	Drinking Water	1
	-	Prague, Czechoslovakia	Drinking Water (polluted sample)	3
	Potomac	Washington, D.C.	Drinking Water	4

Sources:
1 U.S. Environmental Protection Agency 1972
2 Kleoper and Fairless 1972
3 Novak *et al.* 1973
4 Swinnerton 1973, pers. comm.

Sources of Oceanic Additions

Sources of aromatic hydrocarbons to the oceans include ocean dumping of toxic liquid wastes, normal operational discharges of oil tankers, tank cleaning by chemical carriers, accidental spillage of various petro chemical commodities, input by rivers, exchange across air-sea interface near urban areas, and natural seepage of oil and gas.

Benzene and toluene are currently being dumped into the ocean as components of liquid industrial wastes being barged to offshore disposal sites. U.S. Environmental Protection Agency dumping permits (1973) report 1.3 x 10^4 kg/month benzene released into the Gulf of Mexico and 5.2 x 10^5 kg/month toluene being discharged in the Atlantic Ocean off the New Jersey coast (Table 4-30). Greve (1971) reported that 5 percent of tested waste barrels consisted of toluene, and that tons of these toxic barreled wastes were being dumped annually in the North Atlantic Ocean and North Sea.

Operational discharges by chemical tankers directly add aromatic hydrocarbons to shipping lanes. Cleaning of chemical tanks after offloading of bulk chemical commodities involves removal of cargo residues with detergents, with waste mixtures often going overboard after the vessel leaves port. The Intergovernmental Maritime Consultative Organization, hereinafter referred to as IMCO (1972) estimates the magnitude of this discharge worldwide at approximately 240 metric tons each for benzene and toluene (Table 4-31). This reflects a 0.085 percent loss of total toluene shipments (approximately 366 x 10^3 tons annually).

These estimates of total shipments may be low. For example, U.S. Corps of Engineers data (Table 4-32) on shipments of benzene and toluene along the Gulf of Mexico (Intracoastal Waterway) and the Mississippi River suggest that 2.3 x 10^6 tons move annually along these routes alone, five times the IMCO figure. Over 40 percent of the annual U.S. aromatic inventory production is shipped in marine barges and tankers (Table 4-33). Waterborne commerce may cause significant releases of aromatics but the extent of land-based disposal of the residues is also needed for adequate evaluation.

TABLE 4-30

Current EPA Dumping Permits Allowing Regular Discharge of Aromatic Hydrocarbons into the Marine Environment

Compound	Company	Dump Site Location	Depth (m)	Quantity of Aromatics in Industrial Wastes
Benzene	E.I. Dupont Beaumont, Texas	Gulf of Mexico Dump Site Coordinants: 27°44'N28°28'W 94°44'N94°28'W	800	$1/3 \times 10^4$ kg/mon
Toluene	American Cyanamid Linden, New Jersey	Atlantic Ocean Dump Site Coordinants: 39°0'N38°30'W 72°0'N72°30'W	2,000	5.2×10^5 kg/mon

Source: U.S. Environmental Protection Agency Regions II and VI, 1973, pers. comm.

TABLE 4-31

Quantities of Benzene and Toluene Released to the Marine Environment Due to Operational Discharges of Chemical Tankers (Tank Cleaning)

Ocean	Quantity of Discharge (m tons) Single Bottom Tanker Benzene	Quantity of Discharge (m tons) Single Bottom Tanker Toluene	Quantity of Discharge (m tons) Double Bottom Tanker Benzene	Quantity of Discharge (m tons) Double Bottom Tanker Toluene	Total Quantities Benzene	Total Quantities Toluene
Baltic		--	0.2	0.7	0.2	0.7
North Sea	110.5	9.7	7.4	6.9	117.9	16.6
Mediterranean	--	--	--	--	--	--
North Atlantic						
Eastern	--	69.0	--	--	--	69.0
Western	25.5	--	37.5	43.2	63.0	43.2
South Atlantic						
Eastern	--	--	0.6	0.5	0.6	0.5
Western	3.3	3.2	1.8	4.9	5.1	8.1
Caribbean	25.0	12.2	--	3.9	25.0	16.1
North Pacific						
Far East	17.1	30.0	--	--	17.1	30.0
North America	--	19.8	--	1.4	--	21.2

(continued)

TABLE 4-31 (continued)

South Pacific						
South America	0.4	1.1	--	0.8	0.4	1.9
Australia	4.0	0.6	--	0.5	4.0	1.1
Indian Ocean						
Eastern	--	--	--	--	--	0.0
Western	2.0	0.6	--	--	2.0	0.6
Unknown	--	16.8	6.2	8.5	6.2	25.3
Totals	187.8	163.0	53.7	71.3	241.5	234.3

Total Discharges: 241.5 tons or 0.085% of total benzene shipments (279,852 tons)

Source: IMCO 1972.

TABLE 4-32

Quantities of Waterborne Aromatic Hydrocarbon Shipments Along the Gulf of Mexico and Mississipii River-1971 (Benzene and Toluene Combined)

Location	Total Tonnage (Metric Tons)
Gulf Intracoastal Waterway (Total) (Apalachee Bay, Florida to Brownsville, Texas)	1,300,000
Gulf Coast Ports:	
Tampa, Fla.	2,800
Panama City, Fla.	10,000
Pensacola, Fla.	15,000
Mobile, Ala	21,000
Tombigbee River, Ala.	42,000
Pascagoula, Miss.	29,000
Atchafalaya River Waterway, La.	27,000
Red River Waterway, La.	13,000
Gulf Intracoastal Waterway, La. (Morgan City-Port Allen Route)	430,000
Lake Charles, La.	680,000
Calcasieu River and Pass, La.	1,200
Sabine-Neches Waterway, Tex.	1,000,000
Orange, Texas	2,800
Beaumont, Texas	390,000
Port Arthur, Texas	120,000
Houston Ship Channel, Tex.	740,000
Texas City Channel, Tex.	360,000
Chocolate Bayou, Tex.	27,000
San Bernard River, Tex.	26,000
Freeport, Texas	260,000
Matagorda Ship Channel, Tex.	2,200
Victoria Ship Cannel, Tex.	79,000
Corpus Christi, Tex.	190,000
Mississippi River (Minneapolis to Gulf passes)	970,000
Minneapolis to mouth of Missouri R.	160,000
Missouri R. to Ohio R.	210,000
Ohio R. to Baton Rouge	500,000
Baton Rouge to New Orleans	150,000
New Orleans to mouth of Gulf passes	
(Oceangoing)	150,000
(Internal)	310,000

Source: U.S. Army Corps of Engineers 1971.

TABLE 4-33

Relationship between Waterborne Shipments of Benzene and Toluene in U.S. Waters and Total U.S. Inventory (Domestic Production + Imports)

Year	Compound-Source	Quantity (m tons x 10^3)	Total Waterborne Shipments Benzene-Toluene (Combined m tons)	Quantity Shipped (Total Inventory)
1971	Domestic Benzene Production[1]	3,700	2,800	39.5%
	Domestic Toluene Production[1]	2,900		
	Benzene Imports[2]	250		
	Toluene Imports[2]	370		
	Total	7,220		
1968	Domestic Benzene Production[1]	3,400	2,900	49.5%
	Domestic Toluene Production[1]	2,300		
	Benzene Import[2]	110		
	Toluene Imports[2]	100		
	Total	5,910		

Sources:
1 U.S. Tariff Commission 1970, 1973
2 U.S. Bureau of the Census 1967-1972b
3 U.S. Army Corps of Engineers (1971
4 Dawson *et al.* 1970

The amount of oil discharged into the world's oceans from all sources has been estimated to be 2×10^6 tons per year (Study of Critical Environmental Problems, hereinafter referred to as SCEP, 1970). Assuming these oils average 3 percent benzene and toluene, this represents 6×10^4 tons of these compounds released annually. The aromatic content of refined petroleum products tends to be higher than that of crude oils (Wasik and Brown 1973).

Petroleum hydrocarbons, including the light aromatics, escape to the marine environment during the operation of oil tankers. The current trend toward LOT (Load on Top) oil tankers may reduce these releases. Recovery of floating oil residues in ballast tanks does decrease the total quantity of petroleum discharged; but the different water solubilities of benzene and toluene would saturate the discharged ballast waters with aromatics. The problem of preferential aromatic release versus total ballast release in normal operational discharge has not been addressed.

Spillages of bulk aromatic commodities during transportation are generally of local importance due to short-term toxic levels reached. The size and location of releases through accidental losses are not predictable (Table 4-34).

Benzene and toluene have been identified as components of subsurface water, especially near petroleum-bearing strata (Kartsev *et al.* 1969, McAuliffe 1969). Levels of 10.4 ppm benzene and 4.7 ppm toluene were found in subsurface brines by McAuliffe (1969). Kartsev *et al.* (1969) isolated up to 24 ppm benzene and toluene in groundwater from areas with extensive oil and gas deposits. Natural seepage from faulted submarine strata and improper disposal of drilling and oil well brines may introduce some aromatic hydrocarbons to the oceans. The extent of these sources is unknown.

While direct addition of oil products is a major contributor to the hydrocarbon concentrations in the marine environment, contributions from rivers and sewage outfalls also require investigation. The relationship between rainout of atmospheric aromatics and subsequent transport to the oceans by runoff if not known. Production site effluents and terrestrial oil losses may contribute to river loads, as evidenced by the detection of aromatics in the lower Mississippi River are (U.S. Environmental Protection Agency 1972, Anonymous [*Environ. Sci. Tech.*] 1973).

TABLE 4-34

Spill Data for Selected Aromatic Hydrocarbons 1968-1970

Substance	Quantity of Spill	Reason for Spillage
benzene	100 long tons	barge wreck
benzene	10,000 gals.	pumping accident
benzene	200 tons	tank accident
benzene	300 tons	tank barge
benzene	60,000 gals.	barge collision
toluene	1 tank car	tank car derailment

Source: U.S. Congress 1971.

Marine Concentrations

Studies of hydrocarbon levels in the oceans due to human activities have recently been conducted (Barbier *et al.* 1973, Brown *et al.* 1973). The studies provide a crude estimate of natural and human sources; however, the methods used do not provide information on aromatic hydrocarbons. Hydrocarbons categorized as aromatics in these studies are actually alkylated benzenes.

Ocean water samples collected by petroleum tankers following traditional trade routes from the Gulf of Mexico and Caribbean to eastern U.S. ports were analyzed for total hydrocarbon concentrations (Brown *et al.* 1973). These routes and other major world tanker routes were analyzed for the concentration of persistent oils that may result from discharge or spillage by petroleum carriers (Esso Research and Engineering 1973). Measured aromatic hydrocarbon concentrations of 1 to 3 ppb were reported, but these levels refer to the higher molecular weight (14 carbons or more) alkylated aromatics.

Light hydrocarbons (C_3 to C_8, including benzene, toluene, and xylene) varied between 0.1 to 0.7 ppb around production platforms off the Louisiana coast and 0.3 ppb in the open Gulf at both the surface and 200 meters (Koons and Monaghan 1973).

Aromatics in the Sediments

Aromatic hydrocarbons may enter the sediments through sorption to suspended particulates and subsequent fallout through the water column (Resources Technology Corp. 1972). Masar (1964) observed direct sorption of benzene on hydrogen, sodium and calcium bentonite clays at 20 C. Aromatics occur in marine sediments due to operational and accidental discharges during production, transportation, and consumption of petroleum (Tissier 1973). Blumer and Sass (1972) noted that spilled oils entrapped in coastal sediments continued to release the low-boiling point aromatics (including benzene and toluene) into the surrounding water mass during weathering for several years.

OVERVIEW

Benzene and toluene are light volatile liquids with major uses as intermediates in the production of plastics and numerous other organic industrial chemicals. Annual U.S. production of these materials is 4 and 2.8 x 10^6 tons per year, respectively. Assuming that the U.S. produces one-third of world production, we estimate that 12 and 8.4 x 10^6 tons per year, respectively, are produced worldwide. These estimates do not include the benzene and toluene present in gasoline and other products. Substantial quantities of these materials are released into the atmosphere by evaporation and incomplete combustion of refined fuels. Localized direct discharges to the marine environment occur during production, transportation, and handling.

Photochemical degradation of benzene has not been clearly demonstrated; however, laboratory data indicates that toluene does undergo atmospheric oxidation to produce photochemical smog components. Both compounds have been shown to undergo biological degradation by microorganisms and certain vertebrate enzyme systems. We are not able to predict environmental residence time with any degree of accuracy because of the lack of data.

The average level in coastal waters is reported to be less than 1 ppb (8 measurements) in the Gulf of Mexico. Bioaccumulation factors on the order of 20-40 have been calculated for fish.

While atmospheric release is substantial, its relative contribution to observed marine levels is not understood. Direct discharge during marine-related transportation activities is better understood and of more immediate concern.

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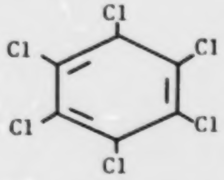
HEXACHLOROBENZENE

Physical Properties

Hexachlorobenzene (HCB) is a white powder that is soluble in benzene, ethyl ether, and chloroform, but relatively insoluble in water and ethyl alcohol. Its empirical formula is C_6Cl_6, its molecular weight is 284.80, and its structure is:



It is to be distinguished from benzene hexachloride, a name frequently applied to the isomers of hexachlorocyclohexane ($C_6H_6Cl_6$). Some physical properties of HCB are:

Melting point:	229 C
Boiling point:	326 C
Vapor Pressure:	1.089×10^{-5} mm Hg at 20 C

The technical grade used in agriculture contains 98 percent hexachlorobenzene, 1.8 percent pentachlorobenzene and 0.2 percent 1,2,4,5-tetrachlorobenzene. Commercial formulations applied as dusts contain 10 to 40 percent HCB and frequently also contain small quantities of lindane (0.5 to 1.0 percent).

Production

The U.S. Tariff Commission Reports include no data on the production or sales of HCB in the United States. Estimates of use as a grain fungicide are available from the U.S. Department of Agriculture. In 1966, application of 0.8 metric tons was reported and in 1971 estimated use increased to 6.9 tons principally in Washington, Oregon and California. No data are available for other years. Two U.S. companies, Dover Manufacturing and Stauffer

Chemical, currently manufacture HCB for fungicidal use (U.S. Environmental Protection Agency 1973).

Statistics on the production and use of HCB in other countries are generally not available.

HCB is a significant contaminant in the pesticides diethyltetrachloroterephthalate and pentachloronitrobenzene. Samples of diethyltetrachloroterephthalate obtained in California have contained up to 10 percent HCB. Environmental releases by this pathway may exceed those of fungicidal use and are believed to be the source of recent HCB contamination of sheep (U.S. Environmental Protection Agency, 1973).

Hexachlorobenzene is a by-product in the manufacture of many chlorinated hydrocarbons, including those produced in large amounts such as perchloroethylene and carbon tetrachloride. The manufacturing processes tend to produce a heavy, tarry by-product which contains a variety of chlorinated compounds, of which HCB is a principal constituent. The tarry residue "hex" waste from perchloroethylene and carbon tetrachloride production is reported to contain 10 to 15 percent HCB (U.S. Environmental Protection Agency 1973). If the amount of HCB produced by this process were equivalent to 0.1 percent of the total production of the low molecular weight chlorinated hydrocarbons, yearly U.S. production would be in excess of 10^3 tons.

HCB is also a by-product in the production of chlorine gas by the electrolysis of sodium chloride (U.S. Environmental Protection Agency, 1973). Estimates of HCB production by this process are not available.

Environmental Release

We assume that all of the HCB used in agriculture and that which is present in preparations of other pesticides as a contaminant enters the environment. Because of its persistence and mobility, HCB enters and is recycled through the biosphere. The industrial tars containing HCB that are waste products in the manufacture of other chlorinated hydrocarbons have been considered immobile and have been deposited in landfills; the first measurements of HCB in air and in soil in the vicinity of these landfills have only recently been accomplished. At the Ascension Parish Landfill in Louisiana, which receives tarry waste from a factory manufacturing low molecular weight chlorinated hydrocarbons, initial determinations recorded 14 ppb (16 ug/m^3) of HCB in air and 0.5 percent HCB in soil (U.S. Environmental Protection Agency, 1973). We consider such landfills to be a source of release because of the mobility of HCB.

Ocean dumping of the wastes of low molecular weight chlorinated hydrocarbon manufacture currently takes place in the Gulf of Mexico (Chapter 5) and in the North and Norwegian Seas (Jensen *et al.* 1970). Although HCB concentrations in these wastes have apparently not been measured, HCB might be a constituent of these wastes. Ocean dumping is therefore a possible path of entry of HCB into the marine environment.

Containment

There are no possibilities of containing the HCB present as a contaminant in pesticidal preparations that are applied directly to the crops. Seed treatment use of HCB entails a period of residence in soil; with time we assume that this HCB will move into the atmosphere. Incineration of the tarry waste products of the manufacture of low molecular weight chlorinated hydrocarbons has been initiated. If this technology can be perfected and implemented, a major source of environmental release would be eliminated.

Persistence

HCB is a very stable unreactive compound. It does not apparently undergo photochemical reactions in the atmosphere, nor is it hydrolyzed in aqueous solutions. There is no evidence that it is broken down by physical or chemical processes in the environment.

Studies of the fate of HCB in organisms indicate it is not metabolized to any significant extent. Pentachlorobenzene is a possible metabolic derivative (Stijve 1971). It appears largely immune to the biological degradation processes (Parke and Williams 1960, Vos *et al.* 1968, Vos *et al.* 1971). The occurrence of HCB in fish and wildlife is an additional indication of its stability in ecosystems.

Mobility

HCB is volatile in water vapor even at low temperatures; co-distillation is therefore a mechanism for dispersal. It also sublimes readily and will evaporate if exposed to air under conditions of adequate ventilation (U.S. Environmental Protection Agency, 1973). Measurement of HCB concentrations in air in the vicinity of a landfill receiving industrial waste from the manufacture of low molecular weight chlorinated hydrocarbons indicate that HCB may enter the atmosphere from such sites (U.S. Environmental Protection Agency, 1973). Aerial dispersal may be the major pathway for HCB entering the marine environment.

Bioaccumulation

Studies carried out at the Fish-Pesticide Research Laboratory in Columbia, Missouri, have shown that *Daphnia magna* rapidly accumulated ^{14}C-labelled HCB from water in a flow-through diluted system. Equilibrium was reached within 24 hours; on a wet weight basis residues in *Daphnia* were 900 times higher than those in the water. When placed in water free of HCB, *D. magna* lost the accumulated residues at a rate corresponding to a half-life of 44 hours. Accumulation of HCB by bluegills fed with HCB-contaminated *Daphnia* was found (Schoettger 1972).

We assume that the bioaccumulation of HCB by aquatic organisms results from a partitioning between the water phase, in which HCB is highly soluble, and the organism. A decrease in water concentrations would therefore result in a decrease in the HCB content of organisms.

Feeding studies have shown that HCB is assimilated from food by sheep (Craig and Dwyer 1961) chickens (Craig 1959, Watts 1968a, 1968b), pigs (Gardiner and Armstrong 1960), Japanese quail (Vos *et al.* 1968, Vos *et al.* 1971), and kestrels (Vos *et al.* 1972). Like many other chlorinated hydrocarbons, HCB is stored in lipids; concentrations in tissues reflect those in the diet and exceed them by factors depending upon lipid content and exposure time.

Field investigations have shown that HCB is distributed among terrestrial and aquatic organisms. Initial investigations were carried out in the Netherlands following the deaths of birds of prey in areas where HCB was being used as a seed dressing (Vos *et al.* 1968). Residue levels in terrestrial ecosystems in the Netherlands have declined following the substitution of another fungicide for HCB (Fuchs *et al.* 1972). HCB has been found in freshwater fish from a number of river systems in the United States (Johnson *et al.* 1973, unpub. ms.) and in New Brunswick, Canada (Zitko 1971) and in the eggs of terns collected in Canada and in the Netherlands (Gilbertson and Reynolds 1972, Holden 1973). Available data for marine species are summarized in Table 4-35.

Toxicity

There are few data on the single dose acute toxicity of hexachlorobenzene (Table 4-37). With a single dose administration HCB has a very low toxicity: 500 mg/kg interperitoneal is nonlethal in rats (Davis *et al.* 1959). The oral lethal dose of a 15 percent suspension of HCB in female Japanese quail is greater than 1 g/kg (Vos *et al.* 1971).

In contrast, the subacute or chronic toxicity of HCB can be significant, (Table 4-36). The most pronounced effect of chronic exposure seems to be dysfunction of the liver.

The impetus for much of the hexachlorobenzene research in recent years came from the outbreak of a cutaneous type of porphyria in southeastern Turkey in 1955 caused by the human consumption of wheat, intended for planting, that had been treated with HCB (Cetingil and Özen 1960, Dogramaci 1961, 1962, 1964, Dogramaci *et al.* 1962a, 1962b, Schmid 1960, Wray *et al.* 1962, Cam and Nigogosyan 1963). The wheat contained about 2 grams of HCB per kilogram of wheat. It was estimated that the persons affected consumed roughly 50 to 200 mg HCB/day for a relatively long period of time before the disease became apparent. The total number of cases between 1955 and 1959 was estimated to be between 3000 and 5000, and the majority were reported in children.

TABLE 4-35

Hexachlorobenzene Residues in Marine Specimens

Species	Source	Number of Specimens	Result			Reference
			Mean	(Units)	Range	
White perch	New Jersey New York	3	0.22	(μg/g wet weight)	0.027-0.56	Johnson *et al.* 1973
Striped bass (*Morone saxatilis*)	Maryland Florida	5	0.038	(μg/g wet weight)	0.011-0.083	Johnson *et al.* 1973
Chinook salmon eggs (*Oncohynchus tshawytscha*)	Oregon	1	0.003	(μg/g wet weight)	-	Johnson *et al.* 1973
Striped bass eggs	Maryland	8	0.23	(μg/g wet weight)	0-1.04	Johnson *et al.* 1973
Striped bass	Florida	1	0.149	(μg/g wet weight)	-	Johnson *et al.* 1973
Cod oil (*Gadus* sp.)	-------	3	0.43	(μg/g wet weight)	0.100-0.63	Johnson *et al.* 1973
Menhaden oil (*Brevoortia* sp.)	-------	1	0.18	(μg/g wet weight)	-	Johnson *et al.* 1973

(continued)

TABLE 4-35 (continued)

American eel *(Angvilla rostrata)*	New Brunswick St. John R.	13	0.012	(µg/g wet weight)	0.006-0.019	Zitko 1971
Eel liver	--------------	4	0.010	(µg/g wet weight)	-	Zitko 1971
Atlantic salmon *(Salmo solar)*	New Brunswick	4	0.002	(µg/g wet weight)	-	Zitko 1971
Herring *(Clupea harengus)*	One sample from Bay of Fundy and 2 from Chedabucto Bay, Nova Scotia	10 10 10	0.006 0.004 0.003	(µg/g wet weight) (µg/g wet weight) (µg/g wet weight)	0.005-0.006 0.003-0.004 0.002-0.004	Zitko 1971 Zitko 1971 Zitko 1971
Mackeral *(Scomber scombus)*	Bay of Fundy	4	0.001	(µg/g wet weight)	-	Zitko 1971
Seal *(Phoca vitulina)*						
Adult bladder	Coastal waters off Netherlands	5	--	(ppm, wet weight)	<0.02-0.09	Koeman *et al.* 1972
Juvenile bladder	Coastal waters off Netherlands	5	0.067	(ppm, wet weight)	(0.040-0.093)	Koeman *et al.* 1972

(continued)

TABLE 4-35 (continued)

Bottle-nosed dolphin (*Tursiopa truncatus)* bladder	Coastal waters off Netherlands	7	--	(ppm, wet weight)	<0.013-0.032	Koeman *et al.* 1972
Harbor porpoise *(Phocoena phocoena)* bladder	Coastal waters off Netherlands	7	--	(ppm, wet weight)	0.01-0.95	Koeman *et al.* 1972

TABLE 4-36

Subacute and Chronic Toxicity of Hexachlorobenzene

Route	Species	Number of Animals	Dose	Duration	Observed Effects	Reference
Oral (in feed)	Rats	5	2 mg/k/day	13 days	No toxic effects.	Gehring and MacDougall 1971
		5	6 mg/kg/day	13 days	Very Light skin twitching and nervousness. Significant incorporation into liver.	"
		5	20 mg/kg/day	13 days	Neurotoxic symptoms. Increase in liver weight.	"
		5	60 mg/kg/day	13 days	Neurotoxic symptoms. Increase in liver and kidney weight.	"
		5	200 mg/kg/day	13 days	Neurotoxic symptoms. Increase in liver and kidney weight.	"
Oral (in feed)	Rats	4	10 mg/kg/day	30 days	No toxic effects.	Kociba *et al.* 1971 Unpublished Ms.

(continued)

TABLE 4-36 (continued)

Oral (in feed)	Rats	4	30 mg/kg/day	30 days	Increase in food consumption and body weight gains, increase in coproporphyrin excretion in urine; liver weight and liver: body weight ratio increased.	Kociba *et al.* 1971 Unpublished Ms.
		4	65 mg/kg/day	30 days	Same as at 30 mg/kg/day.	"
		4	100 mg/kg/day	30 days	Same as 30 mg/kg/day plus elevation in excretion of uroporphyrim.	"
Oral (in feed)	Rats	33	100 mg/kg/day	51 days	13 deaths in one month; neurotoxic symptoms; increased liver weight; porphyria.	Ockner and Schmid 1961
Oral (in feed)	Rats	10	300 mg/kg/day	10 days	30% mortality	Savitskii 1964
		10	50 mg/kg/day	30 days	60% mortality	
		10	50 mg/kg/day	30 days	30% mortality	
Oral (in water)	Rats	13	0.025 mg/kg/day	4 to 8 mos.	No toxic symptoms. Possible effect on conditioned reflexes.	Gurfein and Pavlova 1960*

(continued)

TABLE 4-36 (continued)

Oral (in feed)	Japanese Quail	15	1 ppm	90 days	No toxic effects.	Vos *et al.* 1971
		15	5 ppm	90 days	Slight increase in liver weight; minimal porphyria.	"
		15	20 ppm	90 days	Increased liver weight, decreased egg production; porphyria; liver and kidney pathological changes.	"
		15	80 ppm	90 days	5 deaths (18- to 62-day period); neurotoxic symptoms; porphyria; increased liver weight; decreased egg production and hatchability; liver and kidney pathological changes.	"
Oral (in feed)	Chickens		120-480 ppm in diet	3 mos.	No toxic effects.	Melis 1955
Oral (in feed)	Japanese Quail	12	2500 ppm	30 days	All died in 30 days. (4 died in 7 days.)	Vos *et al.* 1968
		12	500 ppm	30 days	All died within a month.	"
						"

TABLE 4-36 (continued)

	Japanese Quail (continued)	12	100 ppm	3 mos.	Mortality (1-20th day; 10 within 7 weeks; 1-10 weeks). Surviving cock showed marked loss of weight. Necrosis of liver cells; porphyria.	Vos *et al.* 1968
		12	20 ppm			
Oral (in feed)	Guinea-pig		0.5%	8 to 10 days	Marked neurological symptoms.	De Matteis *et al.* 1961
	Mice		0.5%	8 to 10 days	Marked neurological symptoms.	"
Oral (in feed)	Rabbits		0.5%	6 wks.	Increase in urinary porphyrins.	De Matteis *et al.* 1961
			0.5%	8 to 12 wks.	Death occurred	
Oral (in feed)	Male rats	26	0.2%	12 wks.	Retardation in weight gain; porphyria; degenerative changes in the liver.	Campbell 1963

*Portion of table from Gehring and MacDougall 1971

TABLE 4-37

Acute Toxicity of Hexachlorobenzene Following Single Dose Administration

Species	Method of Administration	Minimum Toxic Dose	Average (ppm) Lethal Dose	Total Lethal Dose	Reference
Mice	Oral	400	~4,000	~7,500	Savitskii, 1964
Rats	Oral	500	3,500	6,000	"
Rabbits	Oral		2,600		"
Cats	Oral		1,700		"
Guinea Pigs	Oral		>1,000		Melis, 1955
Bluegill fish	Water		>100		Schoettgar, 1972
Flathead minnows	Water		>100		"
Rainbow trout	Water		>100		"
Channel catfish	Water		>100		"
Rats	Interperitoneal		>500		Davis *et al.* 1959
Guinea Pigs	Oral		>3,000		"
Guinea Pigs	Oral		3,000		Gehring & MacDougall 1971

The principal response to the long-term daily consumption of low levels of hexachlorobenzene by vertebrates is porphyria, which is a manifestation of a disturbance of the metabolic pathway in heme synthesis. The disturbance leads to an increase in the synthesis, accumulation, and excretion of porphyrins, which are intermediates in the synthesis of heme, hemoglobin, myoglobin, cytochromes, and various enzymes. All body cells are involved in the synthesis and utilization of porphyrins, although the erythropoietic system, liver, kidneys, and muscles are particularly active sites.

The clinical manifestations that occurred in Turkey included blistering and epidermolysis of the skin in areas exposed to sunlight; hyperpigmentation; hypertrichosis; increased amounts of urinary and fecal porphyrins; interphalangeal arthritis; hepatomegaly; and an absence of urinary porphobilinogen or of abnormal amounts of delta aminolevulinic acid. Most of the victims were children between the ages of 6 and 15. Dogramaci (1964) indicated that malnutrition, genetic predisposition, and age may influence the susceptibility to the disease. Overt signs of the disease were most frequent in the summer and subsided in the winter. After consumption of the HCB-treated wheat had stopped, the acute skin manifestations disappeared in about 20 or 30 days, and urinary findings reverted to normal in most patients. Relapses in the summer months were often observed. This was explained by the persistence of HCB residues in the body and the tissue-photosensitizing property of the porphyrins. Uroporphyrin exhibits the strongest sensitizing effect, coporphyrin less, and propoporphyrin none.

Following the observation that HCB produces porphyrin in man, the disease was produced clinically in animal experiments with rats, rabbits, mice, guinea pigs, and Japanese quail, (DeMatteis *et al.* 1961, Gajdos and Gajdos-Torok 1961a, 1961b, 1961c, Ockner and Schmid 1961, Wolf *et al.* 1962, Granick 1963, Burnett and Pathak 1964, Pathak and Burnett 1964, Haeger-Aronsen 1964, Pearson and Malkinsen 1965, Granick *et al.* 1966, Cowger and Labbe 1967, Racz and Marks 1969, Mahler and Walsh 1970, San Martin de Viale *et al.* 1970, Vos *et al.* 1971, Strik and Wit 1972, Taljaard *et al.* 1972). Hepatomegaly and liver pathology were observed in all of the experimental species.

Several studies have reported the presence of HCB in human tissues and in human milk. Perirenal fat samples examined in Australia all contained HCB at an average concentration of 1.25 ppm (Brady and Siyali 1972). HCB residues of 6.3 ppm in depot fat and 5.3 ppm in the fat of human milk have been reported in Germany (Acker and Schulte 1970). The range of HCB residues in human adipose tissues from Japan was from 0.30 to 1.48 ppm (Curley *et al.* 1973). Residues in man are therefore frequently above the action guideline of 0.5 ppm in fat established by the Environmental Protection Agency in 1973, or a previous guideline of 0.3 ppm upon which beef was condemned in Louisiana in late 1972 and 20,000 cattle subsequently quarantined (U.S. Environmental Protection Agency, 1973).

OVERVIEW

Hexachlorobenzene (HCB) is a hazard to man and to the environment. It is highly resistant to chemical, biological, and physical degradation; it appears to be readily dispersed through the atmosphere and, like many other chlorinated hydrocarbons with similar properties, is accumulated in food webs. The use of HCB as a fungicide in seed treatment in the Netherlands has resulted in losses of wildlife. In the United States it has been detected in poultry and meat from twenty states; HCB-contaminated cattle in Louisiana have been quarantined. HCB has been detected in human fat and human milk. It is present in several marine ecosystems. Industrial wastes of factories manufacturing other chlorinated hydrocarbons appear to be a major source of HCB releases; these sources could be reduced and probably eliminated by the proper incineration of these wastes. HCB also enters the environment as a contaminant in the pesticides diethyltetrachloroterephthalate and pentachloronitrobenzene.

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ACRYLONITRILE

Acrylonitrile is an intermediate used in the synthesis of a range of compounds. Shortly before and during World War II it was used for nitrile rubber and as a copolymer with butadiene for oil resistant fiber. A variety of uses have developed since that time, but the growth in acrylonitrile production has been almost entirely due to use in acrylic fibers. There is little environmental information on acrylonitrile.

Physical Properties

Acrylonitrile (vinyl cyanide; propeneitrile; cyanoethylene) is a colorless liquid with a faintly pungent odor. It has the chemical formula $H_2C{=}CHCN$ with a molecular weight of 53.06. Acrylonitrile is miscible with most of the common organic solvents including acetone, benzene, carbon tetrachloride, ether, ethyl acetate, ethylene cyanohydrin, methanol, petroleum ether, toluene, xylene, and some kerosenes. It has a water solubility of 5.35 percent at 20 C, and water has a solubility of 3.1 percent in acrylonitrile. The following are some of acrylonitrile's physical properties:

Boiling point:	77.3 C
Freezing point:	-83.55 C
Specific gravity:	0.8060 at 20 C
Vapor density:	1.83 (Air = 1.0)
Viscosity, liquid:	0.34 cP at 24 C
Surface tension:	27.3 dynes/cm at 24 C
Flash point:	0 C (open cup)
Latent heat of vaporization:	7.8 kcal/mole, vapor, 25 C
Latent heat of fusion:	36.20 kcal, mole, vapor 25 C
Refractive index:	1.3888 at 25 C

Vapor pressure:

C°	mm Hg
8.7	50
23.6	100
45.5	250
64.7	500
77.3	760

Dipole moment: 3.3×10^{-18} esu - cm (in CCl_4)

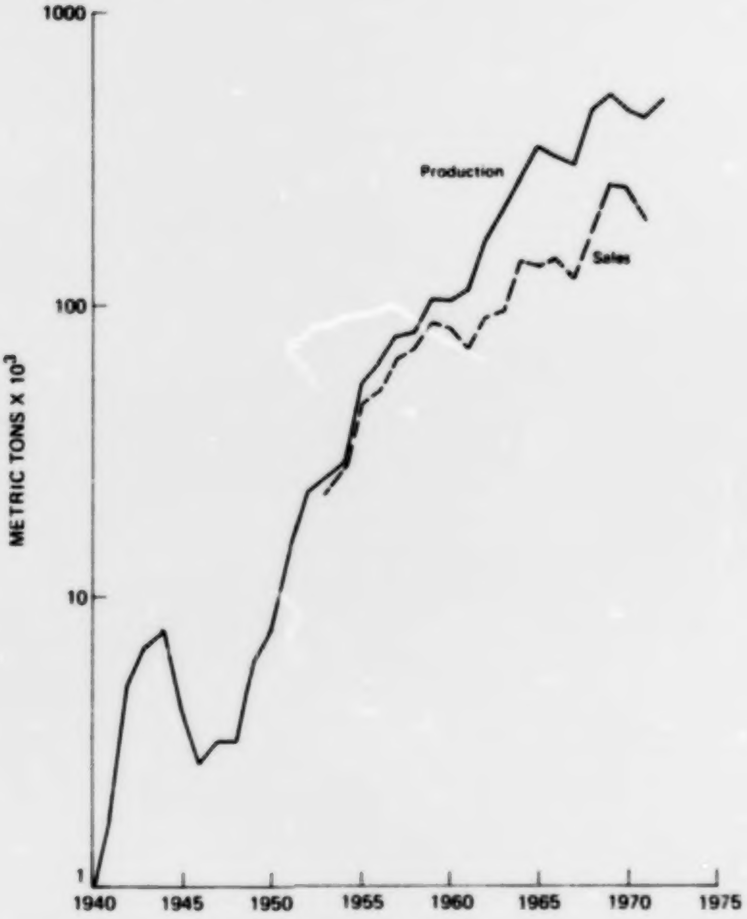
Reactions

Acrylonitrile is a versatile chemical intermediate. Its reactions may involve the cyano group (CN), the activated double bond (C=C) or both groups. It readily reacts with olefins, alcohols, and aldehydes. The nitrile group can also be converted to an amide or organic acids in the presence of acids or bases. The double bond undergoes Diels-Alder and related reactions as well as halogenation and hydrogenation. Highly pure acrylonitrile undergoes polymerization spontaneously. Acrylonitrile polymerizes explosively in the presence of concentrated alkali. A more comprehensive treatment of the reactions of acrylonitrile is found in Chemistry of Acrylonitrile (American Cyanamid Co. 1959).

Production

Commercial production of acrylonitrile was begun in Germany shortly before World War II, and in the U.S. in 1940. Of the commercially produced nitrogen containing compounds, acrylonitrile is second only to urea in production. Recent production has been approximately 5×10^5 metric tons annually growing at a rate of 12 percent per year (Figure 4-14), largely due to the demand for acrylic fibers.

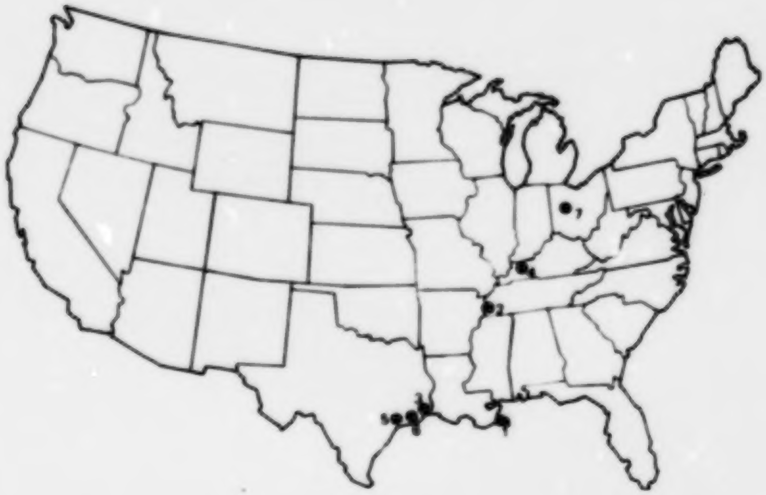
Currently, acrylonitrile is produced by five companies in seven production sites (U.S. Tariff Commission 1971, Stanford Research Institute 1969) (Table 4-38, Figure 4-15). The increasing importance of production of acrylic fibers is indicated by a decline in sales as a percentage of production from approximately 89 percent in



Source: U.S. Tariff Commission 1971

FIGURE 4-14

Production and Sales of Acrylonitrile



Production Sites

1. Frontier, Louisiana
2. Memphis, Tennessee
3. Beaumont, Texas
4. Calvert City, Kentucky
5. Alvin, Texas
6. Texas City, Texas
7. Lima, Ohio

FIGURE 4-15

Production Sites of Acrylonitrile

1955 to 53 percent in 1972. The Chemical Economics Handbook (Stanford Research Institute 1969) lists 37 companies outside of the U.S. producing acrylonitrile. U.S. exports have decreased in recent years as foreign production has increased. The 1972 exports were 2,470 tons or 0.5 percent of total production. The U.S. imports of acrylonitrile, mainly from the United Kingdom and the Netherlands, amounted to 1.1 tons in 1972 (U.S. Bureau of Census 1973).

TABLE 4-38

Producing Companies, Plant Locations, and Production Capacities for Acrylonitrile

Company and Location	Annual Capacity 10^3 Tons	Raw Material
American Cyanamid Company Frontier, Louisiana	90	Propylene-NH_3
E. I. du Pont de Nemours and Company, Inc.		
Memphis, Tennessee	80	Propylene-NH_3
Beaumont, Texas	90	Propylene-NH_3
Monsanto Company		
Alvin, Texas	170	Propylene-NH_3
Texas City, Texas	60	Propylene-NH_3
Vistron Corporation Lima, Ohio	160	Propylene-NH_3

Source: Stanford Research Institute, 1969 (includes estimates of plant capacities coming on stream up to mid-1970).

Manufacturing Process

Acrylonitrile is produced industrially by two processes. Production from the reaction of acetylene and hydrogen cyanide has been used since 1967 only by Monsanto, Co. (Stanford Research Institute 1969). The main production of acrylonitrile comes from the reaction of ammonia with propylene.

Acrylic fibers are produced by the copolymerization of acrylonitrile. Throughout the world different catalytic systems are used in this process, but in the United States only the Sohio process involving the use of a depleted uranium catalyst is used. It does not give a complete conversion and hydrogen cyanide and acetonitrile are by-products of the reactions. The Chemical Economics Handbook (Stanford Research Institute 1969) and Chemistry of Acrylonitrile (American Cyanamid Co. 1959) have reviews of acrylonitrile manufacturing processes.

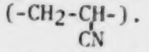
The commercial product is of extremely high purity, impurities other than water are present only in parts per million. The presence of a few tenths of a percent of water improves stability. A few parts per million of a polymerization inhibitor are added to stabilize the product.

Consumption

Acrylic and modacrylic fibers, nitrite elastomers, and plastics account for the majority of acrylonitrile consumption (Figure 4-16):

Consumption of acrylonitrile - 1968

Use	Percent
Acrylic fibers	53
Plastics	11
Nitrile elastomers	6
Exports	18
Miscellaneous	12

Acrylic fibers are composed of at least 85 percent of the acrylonitrile unit  $(-CH_2-\underset{CN}{CH}-)$. Table 4-39 lists U.S. producers of acrylic fibers. Modacrylic fibers contain at least 35 percent by weight of acrylonitrile units. The acrylonitrile consumed in ABS and SAN resins is included in the plastics category. An average ABS resin contains about 25 percent acrylonitrile, and consists of acrylonitrile and styrene on a polybutadiene

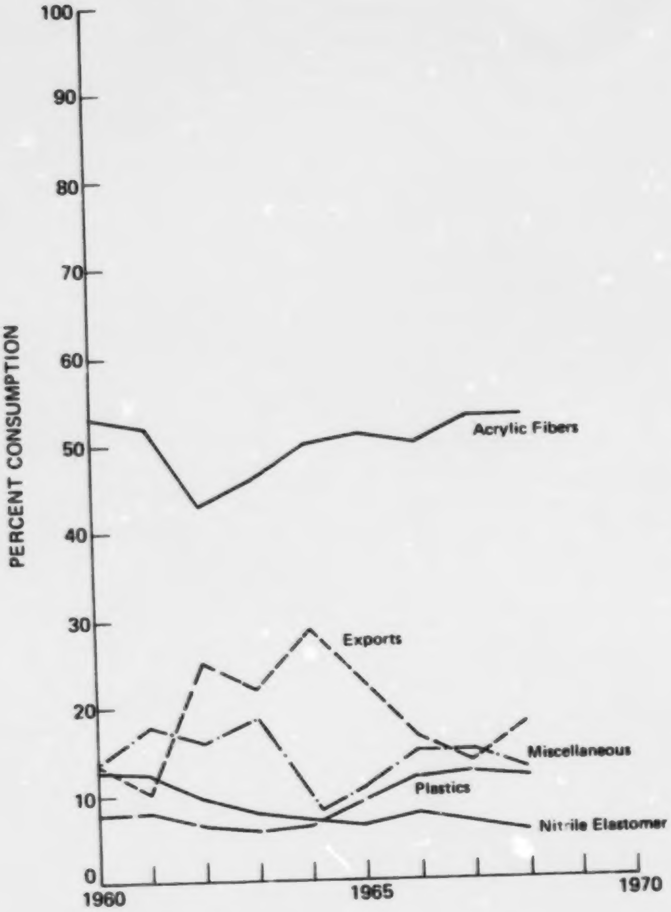


FIGURE 4-16

Consumption of Acrylonitrile

TABLE 4-39

Acrylic Fiber Producers
Companies, Plant Locations, Production, Capacities, and Trade Names

Company	Annual Capacity as of August 1, 1969 (Metric Tons x 10^3)	Primary Registered Trademark
American Cyanamid Co. Pensacola, Florida	35[1]	Creslan
Dow Badische Co. Williamsburg, Virginia	18	Zefraw Zefkrome
E.I. du Pont de Nemours & Co., Inc. Camden, South Carolina Waynesboro, Virginia.	<100	Orlon
Monsanto Company Decatur, Alabama	225	Acrilan
Total	<570	

[1] After 1970, an expansion of 55 x 10^3 metric tons/year is planned.

[2] Courtaulds North America, Inc. planned to build a 22.5 x 10^3 metric ton/year actylic fiber plant in Eastover, South Carolina.

Source: Stanford Research Institute 1969.

base. Numerous resins with different compositions are made and have been used extensively in recent years for automotive parts, pipes, fittings, and in major appliances. SAN resins, copolymers of styrene and acrylonitrile, usually contain 24 to 30 percent acrylonitrile by weight, and are used in glass-filled battery cases, automobile instrument panels, instrument lenses, tumblers, and filaments (Stanford Research Institute 1969).

Nitrile elastomers are copolymers of butadiene and acrylonitrile in which the acrylonitrile content varies between 20 and 50 percent by weight, depending on properties desired. These properties include resistance to chemicals, oils, solvents, heat, aging and abrasion, dielectric properties, and low temperature flexibility. Their uses include hoses, seals, gaskets, belts, brake linings, electrical insulation, nonwoven fabrics, and tank linings.

Miscellaneous uses include starting material in the production of adipontrile [$NC(CH_2)_4CN$] for Nylon 66, and acrylamide ($CH_2=CHCONH_2$) for polyacrylamides used as papermaking strengtheners. Because of its high reactivity acrylonitrile has a number of minor uses, most of which are in organic synthesis. Acrylonitrile has some small-volume farm use as a fumigant to treat grain, dried fruit, walnut, and tobacco, but its high cost and high flammability have deterred extensive use. It is sometimes used as a "spot fumigant" in flour mills and bakeries. Acrylonitrile does not affect the germination of a wide range of vegetable, cereal, and flower seeds; however, it is highly toxic to nursery stock and seriously damages fresh fruit (Food and Agriculture Organization-World Health Organization, hereinafter referred to as FAO-WHO, 1965).

Toxicity to Humans and Animals

Acrylonitrile is toxic to humans by ingestion, inhalation, and contact with the skin. Vapor poisoning usually results in nausea, vomiting, or diarrhea, flushing, headache, salivation, sneezing, altered respiration, weakness, asphyxia, and loss of consciousness (Wilson 1944, Sartorelli 1966). Anemia has been attributed to it, and the liquid may blister the skin (Graham 1965). The American Conference of Governmental Industrial Hygienists has established a TLV of 20 ppm as the maximum allowable concentration in the atmosphere. The level is largely based on acrylonitrile undergoing hydrolysis to HCN.

Several investigators have reported acute and chronic poisoning in animals (Dudley and Neal 1942, Dudley *et al.* 1942, Smyth and Carpenter 1948, McOmie 1949, Brieger *et al.* 1952, Bernes and Cerna 1959, Komissarov 1960, Paulet and Desnos 1961, Paulet *et al.* 1966, Tarkowski 1968, Yoshikawa 1968, Zeller *et al.* 1969, Movsumzade 1970, Wisniewska-Knypl *et al.* 1970, Krysiak and Knoblock 1971, Szabo and Selye 1971, Knoblock *et al.* 1972).

Toxicity to Aquatic Organisms

Garrett (1957) reported a 24-hour median tolerance limit on Pinperch of 24.5 ppm, a minimum concentration for total mortality of 30 ppm, and a maximum concentration at which no deaths occurred of 20 ppm. A maximum safe level for fish of 20 ppm has been reported (Dow Chemical, USA 1973 pers. comm.).

Henderson *et al.* (1960) reported the effect of acrylonitrile on Fathead minnows (*Pimephales promelas*), Bluegills (*Lepomis macrochirus*) and Guppies (*Lebister reticulatus*) (Table 4-40) (Figure 4-17). The toxicity after 96 hours exposure was approximately twice that for 24 hours, indicating that acrylonitrile has a high cumulative or chronic toxicity. The same authors studied the chronic toxicity to Flathead minnows (Table 4-41, Figure 4-17).

Biological Oxidation

Ryckman *et al.* (1966) list acrylonitrile with those compounds that can be removed from aquatic environments by acclimated microorganisms. Acrylonitrile has been over 50 percent oxidized in 10 days and virtually completely oxidized in 20 days to NH_3 using an activated sludge seed (Dow Chemical USA 1973, pers. comm.). The literature on the oxidation of acrylonitrile is summarized in Table 4-42.

Ludzack *et al.* (1959) showed that acrylonitrile was one of the more oxidation resistant nitriles; however, they noted that organisms capable of adapting to nitrile oxidation were common in surface water. Ludzack *et al.* (1959) and Buzzell *et al.* (1968) found that bacteria

TABLE 4-40

Static Bioassay Results of Acrylonitrile

Kind of Fish	Dilution Water	TLm(mg/1) 24 hr.	48 hr.	96 hr.
Flatheads	Hard	32.7	16.7	14.3
Flatheads	Soft	34.3	21.5	18.1
Bluegills	Soft	25.5	14.3	11.8
Guppies	Soft	44.6	33.5	33.5

Source: Henderson *et al.* 1960

TABLE 4-41

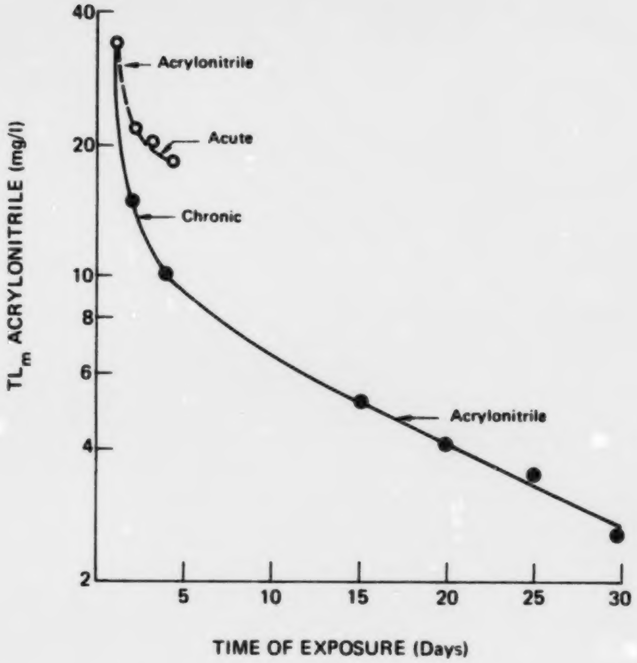
Chronic Toxicity Data for Flathead Minnows*

Acrylonitrile Exposure	TLm(mg/1) Acute	Chronic
24 hours	34.3	33.5
48 hours	21.5	14.8
72 hours	20.3	11.1
96 hours	18.1	10.1
5 days		8.1
10 days		6.9
15 days		5.2
20 days		4.2
25 days		3.5
30 days		2.6

*continuous flow

They also found no tainting of fish flesh was apparent at maximum sublethal concentrations.

Source: Henderson *et al.* 1960



Source: Henderson *et al.* 1960

FIGURE 4-17

Acute and Chronic Toxicity of Acrylonitrile

TABLE 4-42

Biological Oxidation of Acrylonitrile

Technique	Theoretical Oxidation (percent)	Reference
COD, River Water, 2 days Acclimated sludge seed	100	Cherry *et al.* 1956
BOD, aged sewage seed:		
5 days	nil	Ludzack *et al.* 1959
12 days	5	
BOD, Ohio River seed:		
5 days	nil	Ludzack *et al.* 1959
12 days	15	
BOD, River Water, 10 days sewage seed, dispersed seed aeration	67	Mills and Stack 1954
BOD, 10 days sewage seed @ 20°, dispersed seed aeration	28	Mills and Stack 1954
BOD, 30 days sewage seed quiescent conditions	38	Buzzell *et al.* 1968
BOD, 10 days acclimated activated sludge seed, treatment plant conditions	25	Mills and Stack 1954
Chemical analysis-N, 28 days acclimated sludge seed, treatment plant conditions	70	Ludzack *et al.* 1959

required a long time for initial adaptation to acrylonitrile, and for adjustment from summer to winter temperatures. Buzzell *et al.* (1968) using a sewage seed, observed that acrylonitrile degradation had a 12-day lag time in oxidation by the seed organisms. There was little change in O_2 utilization, removal and transformation of carbon, or changes in bacterial populations during the lag time. They showed that nitrile oxidation (excluding lactonitrile) did not lead to the formation of HCN, but to the formation of organic acids and ammonia. Mills and Stack (1954) postulated that the oxidation of acrylonitrile was probably preceded by enzyme hydrolysis of the nitrile groups to the carboxylic acids.

Environmental Considerations

Introduction of acrylonitrile into the environment can occur from losses from production and consumption, direct dispersion as a fumigant, and losses during transportation. The agricultural usage appears to be small enough to be disregarded when considering transport to the oceans, 12.1 tons in 1971 (Berry 1973, pers. comm.) on a global basis. The Intergovernmental Maritime Consultative Organization (IMCO) 1972 estimated the total discharge of acrylonitrile to the sea from transport and handling in 1970 to be 41 tons. The most important source for the introduction of acrylonitrile into the environment is during its production and consumption. The bulk of acrylonitrile is used in production of acrylic fibers and elastomer, and it is estimated that only a small percentage of this is lost. If a 1.5 percent loss is assumed, and if the U.S. production is one-third of world production (Murray and Riley 1973), for which firm data are lacking, the introduction of acrylonitrile into the environment would be approximately 22.5 x 10^3 tons yearly.

There are few reports on concentrations of acrylonitrile in natural water systems or in the atmosphere. Webb *et al.* (1973) reported 100 mg/l of acrylonitrile in an acrylic fiber plant's settling pond. The fate and breakdown of acrylonitrile in the atmosphere and natural waters has not been extensively studied. However, acrylonitrile has been shown to undergo bacterial degradation and loss of acrylonitrile from natural water systems is expected by chemical and biological degradation.

OVERVIEW

Acrylonitrile is produced in large quantities of which 90 to 95 percent is used as an intermediate in the production of polymers. We estimate the amount annually released to the environment to be 22.5 x 10^3 tons. The chemical reactivity and relative biodegradability of this molecule indicate that upon release to the environment it would degrade and have a short residence time. Thus, acrylonitrile should not have any significant impact on maritime organisms, except acute effects of direct high level discharges (spills or uncontrolled plant effluents) to the marine environment, especially estuaries. These conclusions should be tested by a few careful measurements in waters adjacent to transport and production facilities.

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CHAPTER 5

OCEAN DISCHARGE

Workshop Panel

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INTRODUCTION

The waste products of technology reach marine systems through a variety of pathways. These include: the ocean dumping of dredged sediments which may contain pollutants as well as natural materials; the direct discharge of municipal sludges and industrial waste products from barges or ships; and discharge of waste material from cities and industries directly to the oceans through ocean outfalls.

These types of ocean discharge are common in each of the major U.S. Coastal areas, the Pacific, the Gulf of Mexico, and the East Coast including Puerto Rico. The disposal of dredge spoil occurs in all areas. The discharge of municipal sewage sludge by barge dumping is prevalent on the East Coast in the Mid-Atlantic Bight. The disposal of industrial wastes by barge dumping is practiced mainly in the Gulf of Mexico and off the East Coast. The Southern California Bight provided the best available data on the discharge of municipal and industrial effluents through outfalls.

In this section, we excluded river and atmospheric transport of materials. Other pathways of varying degrees of significance by which waste materials reach the oceans but which are also not considered are:

1. the accidental discharge of materials;
2. the discharge of materials as a result of the cleaning of tanks and holds of ships;
3. the discharge of brines, oil, and other materials resulting from offshore oil drilling and production and offshore mining activities;
4. the discharge of sewage from marine commerce and pleasurecraft, and,
5. creation of artificial habitats using waste materials.

LEGAL BASES

In October, 1972, Congress provided additional legislation for Federal control of water pollution: the Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500) and the Marine Protection, Research and Sanctuaries Act of 1972 (Public Law 92-532).

Under P.L. 92-500, discharges of pollutants into navigable waters, which includes the territorial sea and the contiguous zone, are unlawful without a permit. Section 402 establishes the National Pollution Discharge Elimination System (NPDES) for all public and private dischargers to be administered by the Environmental Protection Agency (EPA). Individual states may issue permits under their own program if it is authorized and approved by EPA. Rules and regulations governing the NPDES were published in the Federal Register on May 22, 1973.

Permits for transporting and dumping wastes anywhere in ocean waters are required under P.L. 92-532, effective

April 23, 1973. Interim regulations and criteria governing the issuance of dumping permits were published in the Federal Register on April 5 and May 16, 1973, respectively. Final regulations and criteria were issued October 15, 1973 (38 FR 28610-28621).

On the international level, a "Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter" was approved at an International Conference in London, October 3 to November 13, 1972. The Convention was ratified by the United States on August 3, 1973 (S. 15800) and will become effective following ratification by 15 Contracting Parties (countries).

In March 1974 P.L. 92-532 was amended (P.L 93-254) to incorporate those provisions of the international convention not included in the original legislation.

The London Convention prohibits the dumping of some materials, requires special care for the dumping of other identified substances, and provides for a general permit for others. The prohibited substances (except as trace contaminants) include organohalogen compounds, mercury and cadmium and compounds of these metals, persistent plastics and other persistent synthetic materials, crude oil and certain other petroleum products. Absolutely prohibited are high-level radioactive wastes and materials produced for biological and chemical warfare. The prohibition does not include substances which are rapidly rendered harmless by physical, chemical, or biological processes in the sea, unless they make edible marine organisms unpalatable or endanger human health. The list of materials which require special care includes arsenic, lead, copper, zinc, and their compounds, organosilicone compounds, cyanides, fluorides, and those pesticides not contained in the list of prohibited substances. In addition to these, the disposal of industrial wastes containing large quantities of acids and alkalis are to be assayed for beryllium, chromium, nickel, vanadium, and their compounds.

The regulations adopted by EPA under P.L. 92-532 have been designed to be consistent with the International Convention.

P.L. 92-532 gives responsibility for issuing permits for ocean disposal of dredged material to the U.S. Army

Corps of Engineers, subject to the criteria developed by EPA. Permits for dumping all other materials (e.g. municipal sewage sludge, industrial waste) are issued by EPA. Radiological, chemical, or biological warfare agents, and high-level radioactive waste may not be dumped under any circumstances.

In this study we reviewed permits issued by EPA to August, 1973, under P.L. 92-532 for municipal and industrial wastes to the Middle Atlantic Bight, the Gulf of Mexico, and the deep ocean. We also examined disposal of dredged materials.

The EPA central office in Washington, D.C. allocated the responsibility for permit approval to its ten regional offices. We requested each of the regional offices to provide information on the types and quantities of waste materials discharged.

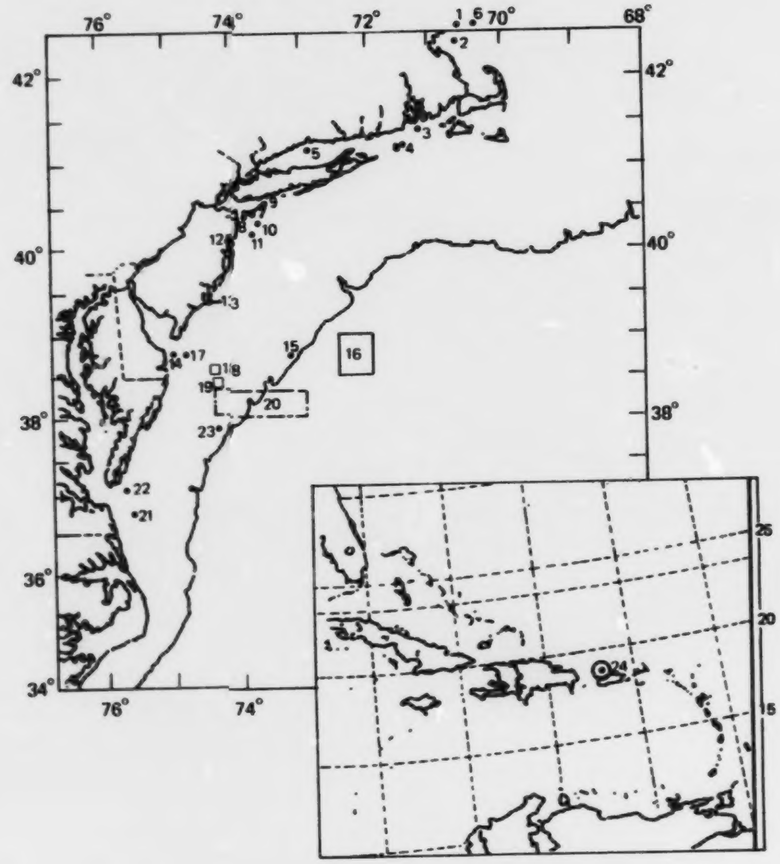
MID-ATLANTIC BIGHT & DEEP OCEAN

From May 1973 to August 9, 1973, EPA issued 42 permits in the Middle Atlantic Bight and off Puerto Rico (Figure 5-1, Table 5-1).

We considered five EPA approved dump sites, referred to herein as the deep-sea sites, as a group (Table 5-1). Four of these sites are located near the outer edge of the continental shelf, from New Jersey to Virginia (Figure 5-1), the shallowest at approximately 1.8×10^3 meters. The fifth site is located over the Puerto Rico trench where the greatest depth (10^4 meters) in the Atlantic Ocean has been recorded (Figure 5-1). The floor of the trench is flat, and the sediment consists of graded calcareous sand which contains shallow-water Foraminifera and the alga Halimeda (Ericson *et al.* 1952). Thus, a transport of surface material to the hadal zone is indicated.

Dredge Spoil and Municipal Sewage Sludge

Although dredge spoil dumping is controlled by the U.S. Army Corps of Engineers, EPA formulates policies for choosing sites and regulations for the disposal of such wastes. Dredge spoils consist of aqueous slurries of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Dump Site Coordinates from EPA Ocean Dumping Criteria, May 16, 1973, Federal Register, Vol. 38, No. 94, Pt. 2.

FIGURE 5-1

EPA East Coast and Deep Ocean Dumping Permit Sites, 1973

TABLE 5-1

EPA Dumping Permits for the East Coast

Northeastern Bight
EPA Region II - New York

Chemical Wastes

Permit Holder	Location	Dumping Site			Material Description	Quantity (Month)
		Map #	Lat.	Long.		
E. I. duPont	Linden, N.J.	10	40°20'	73°45'	Inorganic salt, soluble organic compounds	Less than 4×10^5 4×10^5 kg
Titanium Pigment Division N.L. Industries	South Amboy, N.J.	10	40°20'	73°45'	Spent sulfate solution Dark grey mud (H_2SO_4) ($FeSO_4$)	5.4×10^6 kg (Fe)
Chevron Oil Co.	Perth Amboy, N.J.	16	38°30' 39°0'	72°0' 72°30'	Spent caustic solution from refinery; 3-4% solids; pH greater than 11.0	5.6×10^4 kg (solids)

(continued)

TABLE 5-1 (continued)

American Cyanamid	Linden, N.J.	16	38°30' 39°0'	72°0' 72°30'	Toluene Acrylamide (occasionally present) Malathion, Cygon, Thimet, Cytrolane (Biocides)	5.2×10^5 kg Less than 2.5×10^4 kg Less than 3.1×10^5 kg
Allied Chemical	Morristown, N.J.	10	40°20'	73°45'	HCl Fluoride	2.2×10^6 kg 7.6×10^5 kg
Jonas Disposal Inc.	Bayonne, N.J.	9	40°25'	73°45'	Municipal sludge Industrial sludge	4.4×10^5 kg (solids)
Modern Transportation	South Kearney, N.J.	16	38°30' 39°0'	72°0' 72°30'	Wastes from: Merck-Rahway, N.J. National Can-Piscataway, N.J. Penick & Co. - Montville, N.J. Reheis Chemical - Berkeley Heights, N.J.	2.8×10^3 Cubic meters (No further information)
		9	40°25'	73°45'	Wastes from: American Cyanamic - Bound Brook, N.J.	6.1×10^3 Cubic meters (No further information)

(continued)

TABLE 5-1 (continued)

Modern Transportation (continued)				Central Jersey Septic - Matawan, N.J. Coca-Cola Co. - Hightstown, N.J. Evor-Phillips Leasing Co. - Old Bridge, N.J. Tony Gaess Environmental Service - Passaic, N.J. Carl Gulick, Inc. - Dover, N.J. King Cesspool - Emerson, N.J. Makar Trucking - Mendham N.J. Norda Chemical Co. - Hanover, N.J. G. Redner - Wanaque, N.J. Whippany Paperboard - Whippany, N.J.	
Hess Oil	Woodbridge, N.J.	16	38°30' 72°0' 39°0' 72°30'	Sodium hydroxide Sodium sulfide Sodium naphthenates Sodium mercaptides Sodium phenylates Trace quantities of oils	3.0×10^4 kg Spent caustics

(continued)

TABLE 5-1 (continued)

Municipal Sludge						
City of New York	Port Richmond	9	40°25'	73°45'	Sewage sludge	3.4×10^4 kg
	Rockaway	9	40°25'	73°45'	Sewage sludge	9.1×10^4 kg
	Ward's Island	9	40°25'	73°45'	Sewage sludge	2.8×10^6 kg
	Hunt's Point	9	40°25'	73°45'	Sewage sludge	1.2×10^6 kg
	26th Ward	9	40°25'	73°45'	Sewage sludge	2.2×10^5 kg
	Owl's Head	9	40°25'	73°45'	Sewage sludge	4.9×10^5 kg
	Coney Island	9	40°25'	73°45'	Sewage sludge	4.0×10^5 kg
	New Town Creek	9	40°25'	73°45'	Sewage sludge	3.6×10^6 kg
	Bowery Bay	9	40°25'	73°45'	Sewage sludge	1.2×10^6 kg
	Tallmans Island	9	40°25'	73°45'	Sewage sludge	8.2×10^5 kg
	Jamaica	9	40°25'	73°45'	Sewage sludge	5.0×10^5 kg
West Long Beach	Atlantic Beach, N.Y.	9	40°25'	73°45'	Sewage sludge	1.0×10^4 kg
County of Nassau	Mineola, N.Y.	9	40°25'	73°45'	Sewage sludge	8.2×10^5 kg
County of Westchester	White Plains, N.Y.	9	40°25'	73°45'	Sewage sludge	2.8×10^5 kg

(continued)

TABLE 5-1 (continued)

Essex and Union Counties	Irvington, N.J.	9	40°25' 73°45'	Sewage sludge	4.1×10^{5} kg
Middlesex County	Sayreville, N.J.	9	40°25' 73°45'	Sewage sludge	1.2×10^{6} kg
Bergen County	Little Ferry, N.J.	9	48°25' 73°45'	Sewage sludge	7.7×10^{5} kg
Linden Roselle	Linden, N.J.	9	40°25' 73°45'	Sewage sludge	1.9×10^{5} kg
Middletown	Bedford, N.J.	9	40°25' 73°45'	Sewage sludge	6.3×10^{4} kg
Passaic Valley	Newark, N.J.	9	40°25' 73°45'	Sewage sludge	2.9×10^{6} kg
City of Long Beach	Long Island, N.J.	9	40°25' 73°45'	Sewage sludge	6.8×10^{4} kg
Modern Transportation Co.	South Kearney, N.J.	9	40°25' 73°45'	Sewage sludge	6.7×10^{5} kg
Miscellaneous Permits					
Moran Towing Corp.	New York, N.Y.	8	40°23' 73°49'	Construction Rubble	3.8×10^{4} meters^3
U.S. Army Corps of Engineers	New York, N.Y.	11	40°13' 73°46'	"H.W. Long" (Tug)	-----
Police Department	City of New York		"Approved Site"	Firearms	1.2×10^{4} kg (One dump)

(continued)

TABLE 5-1 (continued)

Police Department	City of Paterson	"Approved Site"			Firearms	9.0×10^2 kg (One dump)
Northeastern Bight EPA Region III (Philadelphia)						
City of Philadelphia	Philadelphia, Pa.	18 19	38°20' 38°35'	74°10' 74°20'	Municipal sludge Municipal sludge	4.5×10^6 kg/mo
City of Camden	Camden, N.J.	18 19	38°20' 38°25'	74°10' 74°20'	Municipal sludge	2.1×10^4 kg/mo
E.I. DuPont de Nemours	Edge Moor, Delaware	18	38°30' 38°35'	74°15' 74°25'	Titanium dioxide wastes	5.2×10^5 kg Iron
Sun Oil	Marcus Hook, Pa.	20	38°0'	73°0'	Oil H_2O emulsion containing trace elements and compounds Spent caustic solution	9.6×10^2 m^3 2.7×10^3 m^3
EPA - Deep Ocean Permits						
Merck Sharp	Puerto Rico	24	19°10'	66°35'	Aqueous solution of inorganic and organic compounds	3.2×10^5

(continued)

TABLE 5-1 (continued)

Oxochem Enterprise Puerto Rico Olefins	Puerto Rico	24	19°10'	66°35'	Sodium butyrate, 8 parts	1.0 x 10^4 cm
					Spent caustic, 1 part	1.0 x 10^3 cm
Pollution Control Industries	Maplewood, N.J.	24	19°20'	66°50'	Wastes from the following companies:	
					Abbott (fermentation wastes)	1.4 x 10^4 (settleable solids)
					Merck (synthetic wastes)	5.6 x 10^4 (suspended solids)
						6.7 x 10^2 (settleable solids)
						6.7 x 10^2 (suspended solids)
					Pfizer (cleaning wastes)	1.8 x 10^5 (dissolved solids)
					Upjohn (synthetic wastes)	1.9 x 10^3 (chloroform)
					Bristol (still bottoms)	Not yet available

[1] From EPA Region II permits.

sediments removed from marine, estuarine, and freshwater areas to improve and maintain navigable waterways and harbors. These sediments consist mainly of sand, silt, and clay, but some, particularly those from harbor maintenance, contain particulate and sorbed organic material largely originating from petroleum, municipal, or industrial waste. Other pollutants commonly contained in harbor sediments include heavy metal in particulate, adsorbed, and chelated forms and solids such as rock, wood, metal, glass, and other debris (Boyd *et al.* 1972).

Dredge spoil accounts for the largest mass of wastes dumped in Atlantic coastal waters, amounting to 28.1 x 10^6 tons* annually in 1968 according to EPA estimates. Approximately 45 percent of the spoil is believed to be polluted (Smith and Brown 1971). The average annual discharge of dredge spoil in the New York Bight between 1964 and 1968 ranged from 3.5 x 10^6 tons (Gross 1972) to 5.5 x 10^6 tons (Sandy Hook Laboratory, National Marine Fisheries Service, hereinafter referred to as SHL, 1972).

Municipal sewage sludge, a slurry of solid waste from primary sedimentation and secondary treatment by the activated sludge or trickling filter process (American Chemical Society 1969), is second to dredge spoil in quantity dumped into the Middle Atlantic Bight. It is thickened by gravity, settling, centrifugation, or flotation to a solids content of 3 to 15 percent (Burd 1968). Oxidizable organic matter is a major component of sewage sludge. Sewage sludge contains an average of 23 percent oxidizable carbon in soluble and particulate form (Gross 1972). The dissolved organics consist mainly of acids and sugars, and the particulate fraction contains proteins, carbohydrates, fats, esters, and unidentified organic matter (Pararas-Carayannis 1973). Unidentified organic matter in dredge spoil is considered to be of petroleum origin, but it sometimes contains sewage solids and industrial wastes (Gross 1972).

In 1968, the Atlantic coastal waters of North America received 4.1 x 10^6 tons of sewage sludge averaging 4.5 percent solids by weight, or 0.18 x 10^6 tons/year of solids

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*All units contained in this report are metric unless indicated otherwise.

(Smith and Brown 1971). The New York-New Jersey metropolitan area contributed about 90 percent of the total (Smith and Brown 1971). Gross (1970a) estimated that an average of 0.15 x 10^6 tons per year of sewage sludge solids was dumped in the New York Bight. Current disposal operations account for 0.22 x 10^6 tons per year of solids (SHL 1972). The Philadelphia area discharges 0.077 x 10^6 tons per year of sewage sludge solids (assuming 13.8 percent solids) at its dump site near the mouth of Delaware Bay. EPA estimates that 0.05 x 10^6 tons per year of sludge solids were dumped in the Philadelphia dump site in 1972 (U.S. Environmental Protection Agency 1972). These estimates are based on volumes stated in EPA dumping permits issued in April and May 1973, and on data on solids concentrations (Smith and Brown 1971).

Sewage sludge analyzed by Gross (1970b) contained 150 times more silver, 10 times more chromium, 50 times more copper, 50 times more lead, 30 times more tin, and 30 times more zinc than sedimentary rocks and soils. Sludges may also contain high concentrations of pesticides; concentrations 10^3 to 10^4 times as high as any other sludge sample were found in samples analyzed from Tallmans Island, New York which contained organochlorine pesticides (U.S. Environmental Protection Agency 1973, pers. comm.) (Table 5-2), indicating that this treatment plant discharges 98 kg/yr of pesticides to the New York Bight.

Based on Ryther's (1969) estimate of the natural productivity of the waters in the disposal area of the New York Bight (100 g carbon/m^2 ocean surface/year), Horne *et al.* (1971) calculated that about 1.2 x 10^4 tons per year of carbon would be "fixed" by phytoplankton in the 125 km^2 disposal area, while current disposal operations are putting about 10^5 tons of carbon per year into the same area.

Gross *et al.* (1971) mapped the distribution of carbon-rich sediments in the New York Bight (Figure 5-2). Uncontaminated sediments collected from the continental shelf more than 10 km from the dumping areas contained less than 0.2 percent total carbon. Gross assumed that sediments containing more than 2 percent total carbon contained organic matter originating in wastes. According to this criterion, waste deposits cover an area in excess of 50 km^2 in the New York Bight. The highest total carbon concentration (6.4 percent) was in sediments near the dredge

TABLE 5-2

Pesticides in Sewage Sludge (mg/1)

Source	γ-BHC	Hepta-chlor	Al-drin	PBC + Hept. Epoxide	Chlordane	PBC Aro-chlor	p,p' DDE	Methyoxy-chlor	DDT	o,p' DDE	Diel-drin	En-drin
Wards Is., N.Y.	---	---	---	46.5(PBC)	---	---	---	---	---	---	---	---
Hunts Pt., N.Y.	4.2	4.5	4.1	11.0(hept. epoxide)	6.1	---	7.0	5.9	6.2	---	---	---
26 Ward, N.Y.	---	---	---	---	---	---	---	---	---	---	---	---
Coney Is., N.Y.	---	---	---	---	---	---	---	---	---	1.5	---	---
Owl's Head, N.Y.	0.5	---	---	---	---	---	---	---	---	---	---	---
Newtown Cr., N.Y.	---	---	---	---	---	---	---	---	---	---	---	---
Jamaica, N.Y.	---	---	---	---	---	---	---	---	---	---	1.44	2.10
Tallmans Is., N.Y.	5,000	32,800	---	≈35,000	12,300	---	20,700	41,500	31,500	---	---	---
Bowery Bay N.Y.	---	---	---	---	---	---	---	---	---	---	---	---
Port Richmond, N.Y.	---	---	---	---	---	68.1	---	---	---	---	---	---

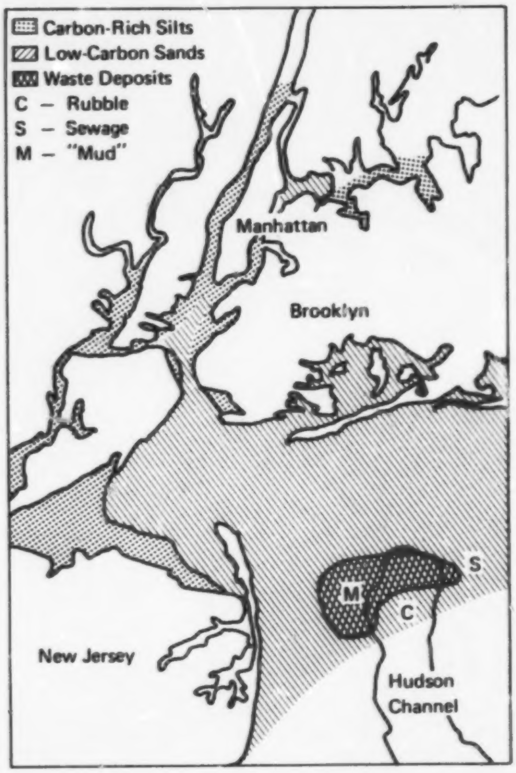
(continued)

TABLE 5-2 (continued)

Rockaway, N.Y.	---	---	---	---	---	---	---	---	---	---	---	---
Passaic Valley N.J.	0.85	---	---	3.5(hept. epoxide)	3.9	---	---	---	---	---	---	---

No biocides were detected other than those given.
Data from analytical reports from Alpha Metals, Inc., Analytical Division.

spoil disposal site. The Sandy Hook Lab (1972) and the Franklin Institute Research Laboratories (Davey 1972) failed to find a buildup of organic matter in the sediments of the Cape Henlopen disposal area. They assumed that the wastes were dispersed in the water column and carried away from the dump site.


Carbon-Rich Silts
Low-Carbon Sands
Waste Deposits
C – Rubble
S – Sewage
M – "Mud"
Manhattan
Brooklyn
New Jersey
M
C
S
Hudson Channel

Source: Pararas-Carayannis 1973 after Gross *et al.* 1973.

FIGURE 5-2

Distribution of Carbon-Rich Deposits in the Harbor and Carbon-Rich Waste Deposits on the Nearby Shelf

Aside from miscellaneous organic compounds, both of petroleum and synthetic origin, the bulk of the organic wastes dumped in the New York Bight and Cape Henlopen (Delaware) sites consists of biodegradable matter of natural origin. Petroleum and synthetic organics may be attacked by microorganisms. Secondary treatment of sewage sludge by aerobic or anaerobic microbial digestion decreases the content of oxidizable organic matter and, hence, the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of the waste. The oxidation process continues after the sludge is dumped. Pararas-Carayannis (1973) suggests that the apparent absence of thick waste deposits in the New York Bight indicates either that the organic matter is rapidly degraded or that a transport mechanism is removing both organic and inorganic sediments.

Degradation of organic matter at the surface of waste deposits and in the water consumes oxygen at a rate between 16 and 330 g O_2/kg of volatile solids (Isaacs 1962).

The difference in oxygen concentration between surface and bottom water of the Bight varies from 2 to 13 mg/l, with the most severe bottom water oxygen depletion occurring between July and October when the thermocline limits natural mixing. The oxygen content of bottom water over the waste deposits is, on the average, two to three mg/l lower than that at the same depth in areas outside of the dumps. In the summer, the oxygen content of bottom waters of the sludge dump reaches 2 mg/l, a level too low to support well-balanced marine life (Pearce 1969).

Another important component of the sewage sludge is its bacterial flora. Buelow *et al.* (1968) found coliform bacteria in sewage sludge in numbers exceeding 2.4×10^9 per 100 ml and fecal coliforms numbering between 4.3×10^5 and 2.4×10^9 per 100 ml. The presence of coliform bacteria and fecal coliforms, in particular, are indicative of contamination with human wastes, and hence, possible presence of human pathogens.

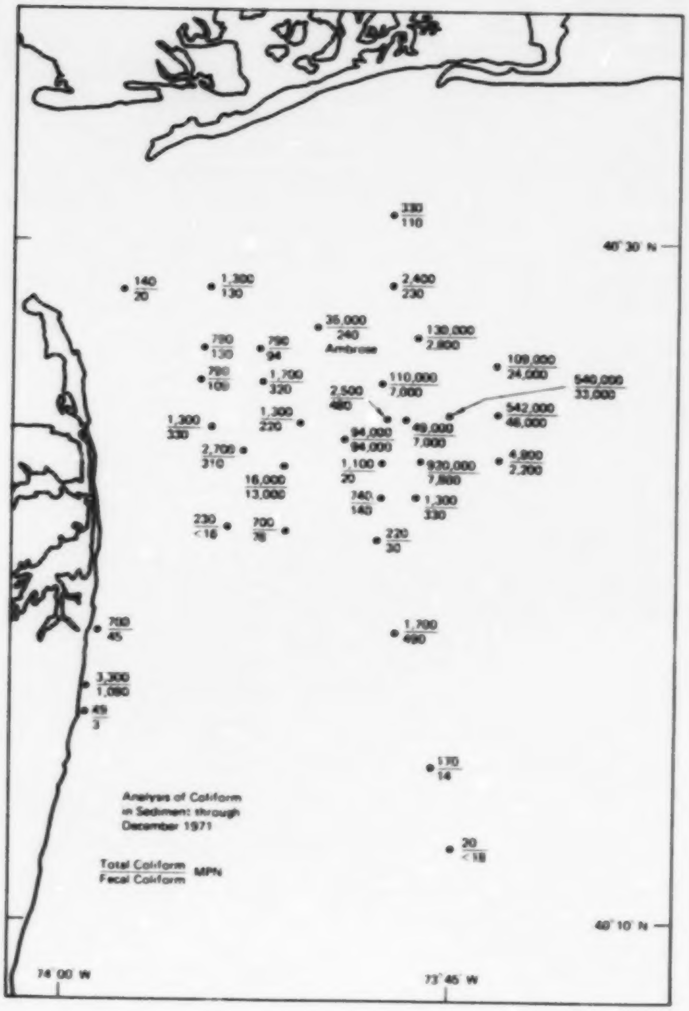
While coliform and fecal coliform counts are useful as indicators of contamination with human wastes, they may not accurately reflect the presence or absence of pathogenic bacteria and viruses in estuarine and oceanic waters. Pathogenic species may survive in ocean water for different periods than the coliform group. Bacteria have been shown to survive in both particulate matter (Hlavka 1971) and marine muds (Greenburg 1956).

Pearce (1969) surveyed the distribution of coliform and fecal coliform bacteria in the New York Bight (Figure 5-3), and found the highest coliform and fecal coliform counts in sediments near the center of the dump sites. Moderate counts were found to extend down into the Hudson Channel, substantiating his contention that wastes are being transported from the dumps down into the Hudson Canyon (SHL 1972). These results indicate that ocean dumping, rather than contaminated river water, is the source of the bacteria.

Clams harvested in the New York Bight for sale have been found to contain 50 to 80 times higher coliform counts than FDA standards (U.S. Council on Environmental Quality 1970). King (1970, unpublished ms.) found excessive coliform counts in more than 80 percent of surf clams collected 8 kilometers from the center of this dump site. However, a similar study of the Cape Henlopen disposal area (Davey 1972) showed that clams were not contaminated with coliform at a distance of 1.6 km from the site. The FDA has closed both sites to fisheries within a 10 km radius as a margin of safety.

We were unable to find a study that attempted to isolate and identify pathogenic bacteria from the sewage sludge disposal area. However, Brezenski *et al.* (1965) state that pathogenic bacteria of the genus *Salmonella*, which includes the causative agent of typhoid and other species which are commonly involved in food poisoning, are often present in sewage sludge and non-chlorinated effluents. These investigators isolated two species, *S. montevideo and S. infantis* from a tidal portion of the Raritan River where the average salinity is about 18 $^{o}/oo$ (parts per thousand). They further state that preliminary results indicate that clams in Raritan Bay are concentrating *Salmonella*. Therefore, it seems possible to us that some *Salmonella* may be concentrated in clams in the vicinity of the sludge dump in the New York Bight.

The Sandy Hook Lab (1972) reports finding fish with fin-rot in the vicinity of the dumping grounds of the Bight. However, they were unable to conclusively demonstrate any relationship to the dumping practices. The Sandy Hook study also found diseased and moribund


330/110
40° 30' N
140/20
1,300/130
2,400/230
35,000/240
Ambrose
130,000/2,800
790/130
790/94
109,000/24,000
790/100
1,700/320
110,000/7,000
2,500/480
540,000/33,000
542,000/46,000
1,300/330
1,300/220
94,000/94,000
49,000/7,000
2,700/310
1,100/20
920,000/7,800
4,800/2,200
16,000/13,000
740/140
1,300/330
230/<18
700/78
220/30
700/45
1,700/490
3,300/1,080
49/3
170/14
Analyses of Coliform in Sediment through December 1971
20/<18
Total Coliform/Fecal Coliform MPN
40° 10' N
74° 00' W
73° 45' W

Source: Sandy Hook Lab 1972

FIGURE 5-3

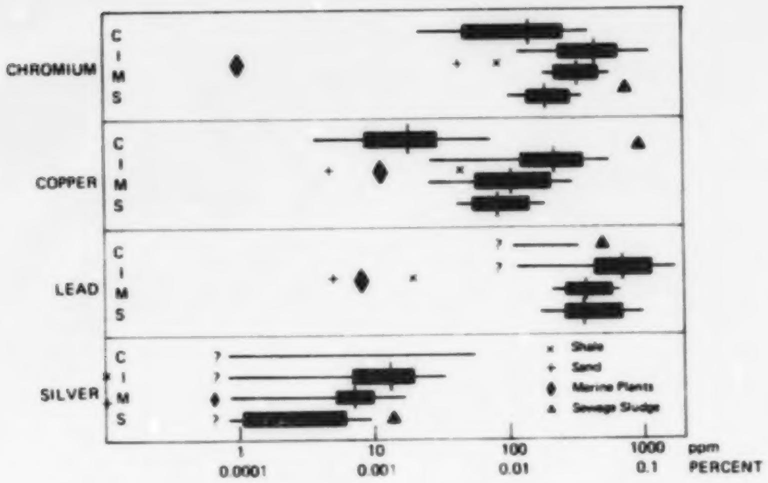
Coliform Analyses from New York Bight Sediments crustaceans in the sludge and spoil beds. Crabs and lobsters placed in aquaria with a sewage sludge substrate developed ulcers and shell erosions and other signs of disease (Pearce 1969). No causative microorganisms were isolated.

Dredge spoil from the area of the New York Bight and from other major metropolitan areas contains high concentrations of various heavy metals (Horne *et al.* 1971). Gross (1972) found high concentrations of silver, chromium, copper, tin, zinc, and lead in sediments composing dredge spoil from the New York area.

In Figure 5-4, the concentrations of chromium, copper, lead and silver in inner harbor sediments of the type constituting New York's dredge spoil, are given and these values are compared with their concentrations in sewage sludge, marine plants, and natural sediments. The metal content of representative samples of sewage sludge from treatment plants in the New York-New Jersey metropolitan area and the Camden-Philadelphia metropolitan area is given in Tables 5-3 and 5-4. The annual input of metals at the dump sites can be estimated from the analytical data and from dumping permits.

The Sandy Hook Laboratory (1972) reported concentrations of heavy metals in spoil and sludge dump sites which were often as high as 100 times the background levels in apparently uncontaminated areas around the dump sites off Barnegat Bay Inlet and in Delaware Bay. The concentrations of heavy metals at the Hudson Channel stations indicate that contaminated sediments are being transported down the Hudson Canyon. Lead was found by Gross (1972) to be the most useful indicator of wastes in the New York Bight. Its distribution correlates well with that of carbon, copper, and silver (Gross *et al.* 1971). Chromium was found in high concentrations throughout the New York Bight. It was particularly abundant in the dredge spoil deposits and in inner-harbor sediments (Gross 1972). Optical emission spectroscopy as used by Gross (1972) does not detect mercury or other volatile metals.

The Franklin Institute Research Laboratory (Davey 1972) reported no significant increases in heavy metal concentrations in the sediments of the Cape Henlopen dump site. The EPA (U.S. Environmental Protection Agency 1972) evaluated the FIRL report and concluded that "contrary to



Median concentration value (indicated by vertical line) range, and limits for 70 percent of samples analyzed (shown by heavy bar) for surficial samples in New York Harbor and New York Bight. (C-continental shelf sediment, I-inner harbor deposits, M-deposits near "mud" disposal area, S-deposits near sewage sludge disposal area). Typical concentrations are shown for shales, sands, and marine plants (Bowen 1966) and sewage sludges. Question marks indicate the detection limits for the various elements.

Source: Gross 1970

FIGURE 5-4 Sediment Metal Concentration, New York

TABLE 5-3

Sewage Sludge Analyses (mg/g solids)

Source	Mercury	Cadmium	Oil by I.R. Percent	Total Solids Percent
Middlesex County[1] NJ	0.046	0.073	0.011	5.570
Bergen County[1] NJ	0.011	0.033	0.004	5.433
Passaic Valley[1] NJ	0.014	0.132	0.010	6.99
Linden-Roselle, NJ	0.0004	0.062	4.00	8.30
Essex & Union Counties, NJ[1]	0.032	0.115	0.002	6.960
Modern Transportation So. Kearney, NJ[1]	0.004	0.055	0.005	3.816
Wards Island, NYC	0.060	0.006	0.065	2.18
Hunts Point, NYC	0.084	0.009	0.132	2.63
26th Ward, NYC	0.048	0.045	0.282	6.61
Jamaica, NYC[1]	0.125	0.053	0.106	3.04
Bowery Bay, NYC[1]	0.062	0.054	0.168	3.295
Coney Island, NYC[1]	0.084	0.017	0.223	5.15
Philadelphia, Pa.				
Northeast:				
Maximum	0.336	0.063	22.0	14.8
Minimum	0.02	0.015	11.2	10.7
Average	0.163	0.028	15.8	12.3
Southwest:				
Maximum	0.210	0.033	9.8	9.3
Minimum	0.071	0.010	5.5	4.9
Average	0.119	0.019	6.8	6.8

[1] When more than one set of analyses were supplied the results were averaged.

Source: Analytical results supplied to EPA regions II and III under terms of dumping permits.

TABLE 5-4

Metal Concentrations in Sewage Sludge (mg/gm dry weight)

Source	As	Pb	Cu	Zn	Se	V	Be	Cr	Ni	Solids Percent
Middlesex County, NJ	0.003	0.212	0.296	0.691	0.0003	<0.004ND	<0.0004ND	0.068	0.043	5.57
Bergen County NJ	0.001	0.596	0.920	5.060	<0.0001ND	<0.003ND	0.0003	6.950	0.187	5.87
Essex & Union Counties NJ	0.001	3.348	4.784	6.580	<0.0001ND	<0.003ND	0.0009	2.701	0.272	6.96
Passaic Valley, NJ	0.0007	2.246	0.106	1.602	<0.0001ND	<0.003ND	0.0003	0.973	0.076	6.99
Wards Island, NYC	*	0.972	2.202	1.835	*	0.055	<0.004	0.624	0.092	2.18
Hunts Point NYC	*	1.080	1.521	1.863	*	0.061	<0.004	0.578	0.182	2.63
26th Ward, NYC	*	0.351	0.333	0.711	*	0.012	<0.002	0.145	0.079	6.61
Jamaica, NYC	*	0.778	1.389	2.569	*	0.031	0.0007	0.375	0.222	2.88

(continued)

TABLE 5-4 (continued)

Bowery Bay, NYC	*	1.084	1.951	2.276	*	0.057	0.0009	1.355	0.347	3.69
Coney Island, NYC	*	1.038	1.385	1.962	*	0.040	0.0007	0.354	0.169	5.2
Philadelphia, Pa.										
Northeast:										
Maximum	NA	4.06	18.1	13.8	3.51	NA		5.63	1.2	14.8
Minimum	NA	2.39	0.60	2.54	0.61	NA		1.06	0.07	10.7
Average	NA	2.957	3.773	6.220	1.458	NA	[2]0.00035	2.145	0.314	12.3
Southwest:										
Maximum	NA	3.3	8.99	6.29	1.68	NA		1.62	3.33	9.3
Minimum	NA	1.75	0.66	2.36	0.22	NA		0.92	0.02	4.9
Average	NA	2.248	2.678	4.14	0.6965	NA		1.236	0.897	6.8

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[1] Percent solid for composite samples is average of values supplied.

[2] Only 1 figure available.

NA: Not Available.

* Concentrations anomalously high for all samples; considered unreliable by analyst.

Source: Analytical results supplied to EPA Regions II and III under term of dumping permits.

assertions in the report, the FIRL study has adduced evidence that a heavy metal containing sediment fraction has been deposited on the bottom in the dumping area. For each of the seven metals investigated the mean for 'inside' is greater than that for 'outside'. The probability that this would occur purely by chance is less than 1 percent--a statistically significant result. Furthermore, a recalculation of the data for copper indicates that the higher mean found for inside the circle is statistically significant ("t" = 2.17 p 0.05)" (Davey 1972, U.S. Environmental Protection Agency 1972).

The contents of metals in sediments of the Cape Henlopen disposal area as reported by Davey (1972) were rarely over 1 ppm, and in no case over 5 ppm. Concentrations of heavy metals in the New York Bight sludge disposal site are on the order of hundreds of parts per million. In view of the similarity in the quantities of these metals being discharged in the two locations, we question where the metals and other components of the waste dumped at Cape Henlopen are going.

Very little is known of the physical and chemical state of metals in dredge spoil and sewage sludge. Gross *et al.* (1971) found that only about one percent of the total metal in waste deposits could be extracted by hydrochloric acid with the exception of nickel, of which five percent was extractable. This phenomenon has been attributed to surface adsorption (Holmes *et al.* 1974), chelation of metal ions by organic materials (Federal Water Pollution Control Administration 1968), and formation of insoluble heavy metal sulfides in anaerobic sediments with high BOD.

In reducing sediments, such as those of the New York Bight, cations of heavy metals are likely to exist as highly insoluble sulfides. Studies of fluxes of cadmium and zinc in Corpus Christi Bay demonstrated that, in the summer when the harbor is most stagnant, these metals are present in the oxidizing surface waters in dissolved states, but in the deeper waters, they react with sulfide ion to form precipitates. In the winter, storms mix and aerate the water, and the oxygen rich water redissolves some of the metals from the sediments. Adsorption on suspended sediment also plays an important part in transport of the metals through the water (Holmes *et al.* 1974). Other investigators had stated that marine bacteria are important in the deposition of heavy metals in estuarine sediments (Oppenheimer 1960, Pomeroy *et al.* 1966, Lowman *et al.* 1971). Ketchum (1970) suggests that heavy metals in sediments may inhibit microbial processes and thereby decrease the rate of waste degradation.

In the New York Bight and perhaps in other areas, ocean dumping of organic and metal-rich wastes creates anaerobic conditions in the sediments, resulting in generation of hydrogen sulfide which forms insoluble salts with heavy metal cations. If the same mechanism is acting as reported in Corpus Christi, dispersal of contaminated sediments by storms and deposition in areas where more oxidizing conditions prevail could cause release of the toxic metals to the waters. Pararas-Carayannis (1973) points out that the data collected by Gross *et al.* (1971) show a decrease in concentrations of heavy metals such as Cr, Pb, Ag, and Cu in the sediments of the dumping sites compared with those of the waters. He suggests that "it is possible that a transfer occurs by lateral loss due to sediment transport, mixing with shelf sediments, or flux to overlying water occurs."

The Sandy Hook Laboratory (1972) found that areas of the New York Bight which were "covered with sewage sludge and dredging spoils were devoid of normal, or are characterized by greatly reduced benthic macrofaunal populations". Meiofauna and macrofauna species diversity and the relative numbers of individuals were diminished, as was the total number of individuals. The meiofauna, especially the foraminifera, were the most ubiquitous organisms in the sediments, occurring even in the most polluted areas.

In other areas, such as between the dredge spoil and sludge dumps, heavy metal concentrations were greatly elevated, but benthic communities were not as severly impoverished as those actually in the dumps (SHL 1972). The Sandy Hook Lab (1972) report gives three reasons for concern with infaunal meiofauna:

1. they are near the base of the benthic food chain;
2. their small size and general immobility would prevent them from extensive horizontal movement, so they should be indicative of the sediment conditions in which they were found; and

3. excluding certain protozoan groups, they are generally the most common group of animals in marine sediments.

Stomach contents of fish collected from the dumps showed that yellow-tail flounder, winter flounder, and red hake mainly eat benthic organisms such as polychaete worms, amphipids, and bivalves, and that they also ingest debris including hair, band-aids, seeds, and cigarette filters. The report states that "the fact that they (fish) are ingesting some of these items opens up the question as to what, if any, of the harmful materials including heavy metals and pathogenic microorganisms are ingested by the "fish".

Investigators of the Sandy Hook Laboratory found petroleum in dredge spoil dumped in the New York Bight (SHL 1972). Sediments in New York Harbor, which accounts for a large portion of that dredge spoil, contain 8 to 10 percent organics (Panuzio 1965) and those in the lower Hudson River contain an average of 5.5 percent (McCrone 1967). Pearce (1969) reported concentrations of hexane extractable material in bottom samples from the dredge spoil dump site in the range 0.5 to 5.0 percent. Analytical results required by EPA permits (Table 5-3) show 0.002 to 4.00 percent oil in sludge samples from New Jersey and 0.065 to 0.282 percent in New York sludge. Philadelphia's sludge contains 11.2 to 22.0 percent hexane extractables from the Northeast Plant and 5.5 to 9.8 percent from the Southwest plant. Hexane extractables include other organics in addition to petroleum products. Organics of petroleum origin may affect marine organisms in three ways: by their toxicity, by their ability to concentrate pesticides, and by their ability to concentrate heavy metals in complexed form (Horne *et al.* 1971).

Horne *et al.* (1971) suggest that the dredge spoil probably contains heavy tars and residues rather than lighter petroleum fractions. Blumer *et al.* (1970) studied an oil spill which occurred near Woods Hole, Massachusetts in 1969. They found that petroleum chemical contaminants persisted in sediments and marine life for at least two years and that the most persistent were highly toxic and carcinogenic aromatic compounds. They further observed that the contaminants spread within the sedimentary column.

Biocides are a major concern from the standpoint of ecological effects because of their high toxicity, their persistence in the environment, and their potential for biomagnification. The organohalogen compounds are important among the biocides. Polychlorinated biphenyls (PCB) are closely related to the organohalogen pesticides in terms of the properties listed above. These lipophilic compounds are absorbed by fatty tissues of marine animals, particularly benthic species such as oysters and clams where they interfere with certain processes of the metabolism of lipids. The organophosphorus pesticides are of the same order of toxicity as the organohalogens, but they are much more quickly degraded in aqueous solution and are, therefore, less likely to accumulate in marine ecosystems.

Pearce (1969) analyzed sediments from the dredge spoil dump site for pesticides and found 0.013 to 0.126 ppm DDT, and the DDT metabolites DDE and DDD, at concentrations of 0.013 to 0.019 ppm and 0.039 to 0.81 ppm respectively. Analytical data on pesticides in sewage sludge from EPA Region II are presented in Table 5-2. Most of the samples contained organohalogen pesticides in the parts per trillion range (ng/l), but the sample from the Tallmans Island facility contained 7 halogenated hydrocarbons in concentrations ranging from 5 to 350 parts per billion (μg/l).

In view of the observations by Seba and Corcoran (1969) that pesticides are concentrated by oil slicks on the sea surface, monitoring of pesticides in the dumping grounds should include sampling of slicks produced by disposal operations.

The organophosphorus pesticides are readily hydrolyzed in basic solution to products which lack the anticholinesterase activity of the parent compounds. However, Bender (1969) found that diethylfumarate, a product of the hydrolysis of malathion, is three times as toxic to fathead minnows (*Pimephales promelas rafinesque*) as the parent compound. Moreover, the toxicities of malathion and diethylfunarate are synergistic (Bender 1969). Similar results were reported for the carbamate pesticide Carbaryl, which hydrolyzed to release 1-naphthol. The hydrolysis product was less toxic to crustaceans but equally or more toxic to mollusks and considerably more toxic to perch than the parent molecule (Steward *et al.* 1967). These studies indicate that the effects of degradation products as well as additive or synergistic effects of toxic compounds should be considered before it is concluded that degradation is equivalent to detoxification.

Horne *et al.* (1971) report that dredge spoil disposal has an appreciable effect on biota over an area of 18 km^2 in the New York Bight, where the average accumulation of dredge spoil amounted to 32 cm/yr between 1964 and 1968. Sludge disposal accounted for a sedimentation rate of about 4 mm/yr over an area of 36 km^2 (Pearce 1969). The authors state that "an accumulation as great as 30 cm/yr may be great enough to exterminate certain benthic organisms simply by burial" (Horne *et al.* 1971).

A study of spoil dumping operations in Rhode Island Sound, where a total of 6.8×10^6 cubic meters of dredge spoil had been dumped, found direct effects of the dumping to be limited. Most mollusks were able to dig out from the periodic burial. Ocean quahogs (*Mercenaria mercenaria*) were present only near the center of the 4.9 to 5.5 meter high spoil mounds. Tube-building amphipods and worms quickly recolonize the spoil dumps (Saila *et al.* 1971).

A study of shallow-water dredge spoil disposal in the upper Chesapeake Bay found significant loss of bottom animals due to burial, but there was rapid recolonization by certain species which returned to pre-dredging levels within 18 months. The sediments covered an area at least five times larger than the designated disposal area (Cronin *et al.* 1967). A study of other dredge spoil disposal areas in the lower Chesapeake Bay area indicated similar conclusions. Recolonization of infauna and epifauna was so rapid that only transitory effects were observed. The same study included observations for sediment buildup in an oyster bed 1.4 to 3.2 km from the discharge point. No dredge spoil accumulation or abnormal mortality of the oysters could be detected (Harrison 1967).

On the whole, the sedimentation effects of dredge spoil dumping were confined to a relatively small area in the immediate vicinity of the dump site and, in the case of non-polluted spoil, were quickly reversible by recolonization with the same bottom communities as previously present or by development of new bottom communities depending on the nature of the dredged sediment.

Therefore, no widespread harm would be likely to result from continued ocean dumping of nonpolluted dredge spoil if the material were thinly enough distributed and did not significantly alter a unique or rare habitat. Presently established dump sites could continue to be used, but future locations should be chosen so that indigenous bottom communities are of a common and widely distributed type to avoid the danger of burying and thus destroying a unique ecological niche.

The amount of turbidity produced by a load of dredge spoil or sewage sludge varies with the size and density of the sediment particles of which the waste is composed. Fine-grained sediments and those with low density will remain in suspension for a longer time than coarser and denser particulates. Dredge spoil from the New York metropolitan area is composed of particles of varying sizes with grain densities between 1.9 and 2.8 g/cm^3, while sewage sludge is composed primarily of fine particulate matter (Horne *et al.* 1971), with an average organic content of about 50 percent and a relatively low grain density of 1.3 to 1.7 g/cm^3 (Gross 1972). Tables 5-5 and 5-6 give particle size ranges and grain densities of various dredged sediments, and Table 5-7 gives organic content (loss of ignition) and grain density of sewage sludge solids. Saila *et al.* (1968) estimated, from studies of dredge spoil dumping in Rhode Island Sound, that up to 25 percent of the dumped material remains suspended for a time in the water while the remaining 75 percent or more settles to the bottom quickly. They observed the formation of two turbidity slicks made up of fine particulate matter. One slick formed at the surface, and a second, which probably resulted from the density gradient at the thermocline formed near mid-depth (Saila *et al.* 1968). The slicks were observed to dissipate after four to five hours, but one to five percent of the sediment remained in suspension for a longer period. A larger portion of sewage sludge solids than of dredge spoil will probably remain in suspension after a dump. Therefore, a significant portion of a load of waste may be carried outside of the specified dump by currents before settling out. The suspended matter is likely to be composed of low density particulates such as organics and oil droplets (Saila *et al.* 1968). This may be an important mechanism for transportation of polluted matter to other areas.

TABLE 5-5

Physical Properties of Dredged Sediments from the New York Metropolitan Region

Material	Typical Bulk Density (tons/meter^3)	Median Grain Size (microns) (Range in Parentheses)
Hudson River Silt	0.65	54 (30-65)
Raritan River Silt	0.65	9 (8.28)
Ambrose Channel Sand	1.6	150 (160-240)
Southern Long Island	1.6	400 (200-53)

Source: Horne *et al.* 1971, data from Gross 1969.

The Franklin Institute Report (Davey 1972) on the Cape Henlopen sludge dump site states that "examination of the drift of digested sludge indicates that the particulates remain in suspension for a considerable time and that the material is well dispersed." The transport and dispersal of a turbidity cloud from a sludge discharge was observed for two hours. The sediment concentration decreased from 10^4 ppm to 25 ppm in 76 minutes and to 10 ppm in 2 hours. A surface cloud was carried over 0.8 km downwind during the observations, and a second cloud at mid-depth was carried "several hundred feet" in the opposite direction. Frequently, a slick of organic matter and debris is associated with sludge dumps in the New York Bight (SHL 1972), and there is no reason to expect that Philadelphia's sludge would have very different characteristics.

The SHL report states that "similar materials were observed in slicks covering square miles of ocean surface" in the New York Bight.

TABLE 5-6

Physical Properties of Dredged Sediment from the New York Metropolitan Area

Dredged Area (Years of Observation)	Median Grain Size (Microns)	Grain Density (g/cm^3)[2]	Sediment Density In Place (g/cm^3)	Porosity Percent
Hudson River (1955-68)	--	2.63	---	--
	44	2.64	1.24	85
	65	2.69	1.24	--
	28	2.66	1.43	73
Lower Bay[1] (1954-67)	55	2.55	1.34	78
	110	2.69	1.40	75
	46	----	1.3	79
New York-New Jersey Channels (1958-67)	350	2.79	1.43	--
	41	2.69	1.31	80
Raritan River (1958-67)	9	2.62	1.42	75
Ambrose Channel (1956-68)	160	2.625	2.09	32
	220	2.636	1.82	50
Sandy Hook Channel (1960-68)	250	1.89	1.89	47
	220	1.98	----	42
South Shore Long Island (1955-68)	530	2.67	2.07	38
	410	----	1.92	40
	270	----	1.98	42

[1] Loss on Ignition: 15.4%
13.0%
2.3%

[2] One gram per cubic centimeter is equivalent to one metric ton per cubic meter or 62.4 pounds per cubic foot.

Source: Horne *et al.* 1971

TABLE 5-7

Physical and Chemical Properties of Waste Solids, New York Metropolitan Region

	Loss on Ignition (Percent)	Grain Density (Percent)
Sewage sludge		
Red Bank, NJ	47.5	1.38
Jamaica Bay, NYC	54.0	1.66
Owl's Head, NYC	49.01	1.32
Rockaway, NYC	47.7	1.86
26th Ward, NYC	50.2	1.73
Coney Island, NYC	55.4	1.71
Average	50.6	1.61

Source: Gross 1972

In the New York Bight, resuspension of the fine sediments by wave action generates turbidity clouds which may carry contamination away from the disposal site. Storms in the New York Bight are capable of producing vertical homogeneity in the water column (Ketchum *et al.* 1951) and of transporting contaminated sediments (Pearce 1969, Horne *et al.* 1971). Horne *et al.* (1971) state that the sludge-contaminated area appears to be spreading toward the northeast and east. Pararas-Carayannis (1973) states that "turbidity currents probably play an important role in the removal of waste sediment" in the New York Bight, and he suggests that the Hudson Channel may conduct such sediments to deeper water in the form of density currents.

Aside from the potential for carrying contamination to areas outside of the dumping grounds, the generation of turbidity clouds may produce other environmental effects. Hollis *et al.* (1964) state that high turbidity can be detrimental to aquatic life, and Saila *et al.* (1968) give nine potential indirect effects of turbidity and siltation on aquatic organisms:

1. reduction in light penetration and reduced photosynthesis;
2. reduction of visibility to some feeding organisms;
3. destruction of spawning areas;
4. reduction of food supplies;
5. reduction of vegetational cover;
6. trapping of organic matter, resulting in anaerobic bottom conditions;
7. flocculation of planktonic algae;
8. absorption or adsorption of organic matter or inorganic ions;
9. adsorption of oil.

Suspended sediment, if sufficiently concentrated, may clog gills and impair respiratory exchange in fish and invertebrates, and it may reduce the growth and survival of larval states of fish and shellfish (Horne *et al.* 1971). Klein (1962) reports that fine suspended solid matter adversely, sometimes lethally, affects the gill epithelium of fish, and Horne *et al.* (1971) state that deleterious effects are to be expected in invertebrates, particularly filter feeders. Studies by Davis (1960) and Loosanoff (1962) on the effects of turbidity on eggs, larvae, and adults of pelecypod mollusks indicated that larval and adult forms will be adversely affected by fine suspended sediment concentrations of 3 to 4 ppt (Saila *et al.* 1968). The University of Rhode Island report on dredge-spoil dumping in Rhode Island Sound stated that fish and lobsters could withstand the high concentrations of suspended sediments for short periods and that lobstering was the least affected fishery in the area (Pararas-Carayannis 1973). The Chesapeake Biological Lab dredging report stated that no gross effects were observed on microscopic plants and animals, on fish eggs or larvae, or on adult fish either held in cages near the disposal point or caught in the area (Cronin *et al.* 1967). The Sandy Hook Laboratory's report on the New York Bight dumping grounds described crabs taken from the disposal site as being moribund and stated that their gills were fouled with granular materials (SHL 1972). The sediments in the sampling area are known to be highly polluted and the reported fouling may have resulted from the pollution load rather than from the sediment itself. Lobsters and crabs kept in aquaria with sewage sludge developed granular fouling and a brown coating which covered the exoskeleton (Pearce 1969). Saila *et al.* (1968) in a turbidity bioassay of lobster for the Rhode Island Sound study observed one case of unusually high mortality which he attributed to some unknown pollutant in the dredge spoil.

Industrial Wastes

In excess of 0.1×10^6 tons per year of industrial wastes are currently being dumped in the Middle Atlantic Bight under permits issued by EPA Region II. Over 90 percent of the industrial waste barged from New York City is acid-iron waste from the titanium dioxide pigment industry (Smith and Brown 1971). EPA Region II has also authorized the dumping of more than 6×10^6 tons per year of industrial waste solids near Puerto Rico. In addition, 8.9×10^3 cubic meters of wastes of unknown composition are discharged in the Middle Atlantic Bight, and 3.2×10^6 cubic meters of solvents from pharmaceutical production are dumped in the Puerto Rico trench.

The composition of industrial wastes is as varied as the processes which produce them. The major industries currently using ocean disposal under EPA permits produce petroleum, chemicals, and pharmaceuticals. The chemical descriptions of these wastes are given in varying degrees of thoroughness.

Approximately 7×10^3 tons per day of spent sulfuric acid solution and mud produced in the extraction of titanium from ore are being dumped in the Mid-Atlantic Bight. The titanium pigment wastes are discussed in Chapter 6. The liquid waste consists of a solution of approximately 8 to 9 percent each of H_2SO_4 and $FeSO_4$ (New York Times

1973) (Table 5-1). Waste from a titanium dioxide plant at Edge Moor, Delaware, has also been dumped at location 18 (Figure 5-1) since July 1, 1969. Only the liquid waste is dumped; the solids are placed in landfill. The permit allows up to 20 barge loads of 4.5×10^3 tons per month.

The effluents of the Grasselli plant in Linden, N.J. are described as "a water solution of inorganic salt containing less than 2 percent of soluble organic compounds." The nature of the organic matter is not mentioned, therefore, we were unable to evaluate its effects on the marine system.

Another waste acid dumped in this area is a liquid containing 27 to 31 percent HCl and 0.5 to 1.5 percent fluoride. It is generated in the manufacture of chlorinated and fluorinated methanes and tetrafluoroethylene and contains 200 ppb of the products.

Four companies, Chevron Oil Co., Hess Oil Co., Sun Oil Co., and Puerto Rico Olefins, have permits to dump wastes in the Atlantic Ocean. Quantities and descriptions of the various wastes are presented in Table 5-1.

Refinery wastes consist mainly of spent caustic solutions which contain sodium hydroxide, sodium sulfide, sodium naphthenates, sodium phenylates, sodium mercaptides, oil (2 percent from one refinery), and between three and five percent solids.

Both Hess and Chevron wastes are spent caustic and are dumped in deep water at site 16, Figure 5-1. Waste from the Sun Oil Company is dumped offshore in relatively deep water at site 20, Figure 5-1. The effluent is a mixture of an oil-water emulsion containing trace elements and compounds and spent caustic solution (Table 5-1). The permit allows disposal of 9.3×10^5 liters per month of a "stable oil in water emulsion containing about 2 percent oil." This amounts to 19 tons of oil per month.

The waste from Puerto Rico Olefins is discharged to the deep water dump site shown in Figure 5-1. Puerto Rico Olefin's spent caustic is combined with a sodium butyrate solution from Oxochem Enterprises. Quantities are shown in Table 5-1.

Approximately 3.2 x 10^6 cubic meters per year of solutions from pharmaceutical production are disposed of in deep water north of Puerto Rico, plus 6 x 10^6 tons per year of solids (Table 5-1). The permits describe the materials dumped as primarily dissolved and suspended solids, with large quantities of iron present in the wastes (6.7 x 10^2 kg per month). The same barge is used to transport the combined wastes to the disposal area.

American Cyanamid presently disposes of a two-phase (toluene and water) waste in the deep ocean at site 16 (Figure 5-1). Included in the waste are the organophosphorus pesticides Malathion, Cygon, Thimet, and Cytrolane, which act as cholinesterase inhibitors (Merck Index 1968). The permit allows the disposal of up to 310 tons per month. For the purpose of renewal of the EPA Interim Ocean Disposal Permit, American Cyanamid performed analysis of their wastes and submitted the results to EPA Region II (Table 5-8). The analytical results do not indicate whether the concentrations of pesticides reported were measured in the aqueous or toluene phase, or whether they are representative of the entire barge load.

Each month approximately 9 x 10^3 cubic meters of mixed liquid wastes, plus 4.4 x 10^5 kg of municipal and industrial sludge solids, may be disposed of by two corporations that serve as disposal agencies. Of this quantity, approximately 3 x 10^3 cubic meters are disposed of in deep water (site 16, Figure 5-1), the rest in relatively shallow water (site 9, Figure 5-1).

The mixed materials handled by Modern Transportation Co., and Jonas Disposal, Inc. originate from a variety of sources (Table 5-1). We were unable to obtain analyses of these wastes.

We found the chemical descriptions of the industrial wastes and the available toxicity data to be inadequate for evaluation or prediction of impacts on the marine system.

Other Wastes

One EPA permit provides for the dumping of construction rubble in the New York Bight at the "cellar dirt" site at a rate of 0.46 x 10^6 cubic meters per year. Two

TABLE 5-8

Partial American Cyanamid Waste Analysis

	Barge I	Barge II	Barge III	Barge IV	Barge V
Arsenic (ppb)	2,600	485	1,445	1,275	700
Total solids (ppm)	85,435	118,120	77,885	109,280	80,977
Malathion (ppm)	1,895	725	1,995	2,055	25
Thimet (ppm)	1,075	815	1,155	1,530	66
Cygon (ppm)	10	5	10	10	0
Cytrolane (ppm)	525	240	1,450	1,140	668
Total Pesticide (ppm)	3,505	1,785	4,610	4,735	759
Bioassay, TL_{50} (ppm)	Not run	Not run	890	2,775	1,700

Source: U.S. Environmental Protection Agency Region II 1973, pers. comm.

permits provide for the one-time disposal of confiscated "dangerous weapons and/or objects" in an "approved site." The Corps of Engineers holds a permit for the disposal of a derelict tugboat and "any additional sunken vessels which are deemed to be obstructions to navigation", upon EPA approval, in the New York Bight wreck disposal site. The permit requires that "all crude oil, fuel oil, heavy diesel oil, lubricating oils, hydraulic fluids, and/or any fixtures containing the above shall be removed." In addition, loose floatable materials must be removed or secured prior to disposal.

GULF OF MEXICO

Fourteen interim disposal sites were approved in the Gulf of Mexico (Federal Register 1973) (Table 5-9 and Figure 5-5), with two classified as chemical disposal areas and the remainder as dredge spoil sites. As of July 1973, four companies with plants at seven locations were using the two areas referred to as A and B in Figure 5-5. The plant locations of these companies and relevant permit information describing the waste materials and method of disposal are listed in Table 5-10.

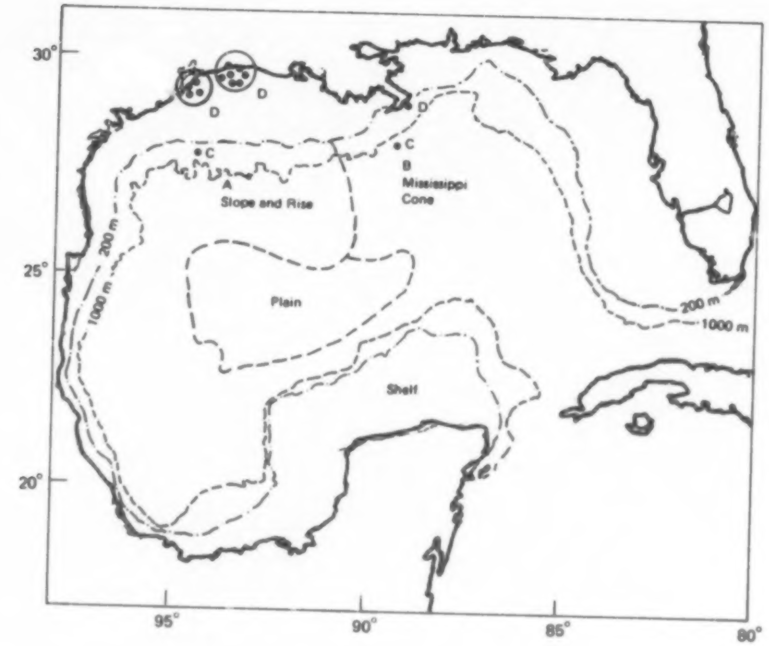
Disposal Site A is situated on the upper part of the Texas-Louisiana continental shelf, approximately 125 miles southeast of Galveston, Texas. Disposal Site B is located off the western side of the Mississippi Delta, approximately 60 miles south of the mouth of the Mississippi River.

The surface circulation pattern of the Gulf consists of a clockwise loop current flowing from the Yucatan to the Florida Straits in the Eastern section and minor, semi-permanent currents in the western section (the areas of dumping). Based on a comparison of six separate north-south transverses across the western Gulf, the winter pattern of east-west surface flow may be characterized by a broad westward flow through the southern section of the Gulf and a narrow zone of stronger eastward flow in the deep-water portion of the northern Gulf (Nowlin 1971). The average direction of water movement over the Texas-Louisiana continental shelf is westward at approximately 1 knot.

TABLE 5-9

Gulf of Mexico: EPA Authorized Dumping Sites, August 1973

Location	Lat.	Long.	Size (sq. km.)	Depth (meters)	Use
Calcasiue Pass	29°45'	93°21'	2.6	2+	Dredging Spoils
Calcasiue Pass	29°45'	93°20'	2.6	2+	Dredging Spoils
Calcasiue Pass	29°42'	93°21'	13.0	6+	Dredging Spoils
Calcasiue Pass	29°35'	93°17'	13.0	6+	Dredging Spoils
Southwest Pass	28°52'	89°31'	5.2	15+	Dredging Spoils
Sabine Pass	29°37'	93°50'	13.0	8	Dreding Spoils
Sabine Pass	29°37'	93°48'	≈7.8	10	Dredging Spoils
Sabine Pass	29°40'	93°51'	≈10.4	2	Dredging Spoils
Galveston	29°19'	94°40'	≈6.5	12	Dredging Spoils
Galveston	29°20'	94°39'	≈6.5	10	Dredging Spoils
Galveston	29°17'	92°40'	18.0	12	Dredging Spoils
Galveston	29°22'	49°43'	≈21.0	4	Dredging Spoils
Waste Area	27°44' 94°44'	27°28' 94°28'	665.0	800	Chemical
Waste Area	28°15' 89°15'	89°35' 89°35'	1040.0	800+	Chemical


30°
25°
20°
95°
90°
85°
80°
D
D
D
C
C
A
Slope and Rise
B
Mississippi Cone
Plain
Shelf
200 m
1000 m
200 m
1000 m

D = Dredge Spoil

C = Chemical Wastes

FIGURE 5-5

EPA Interim-Approved Disposal Sites, Gulf of Mexico

TABLE 5-10

EPA Interim Approved Permits, Gulf of Mexico

Ethyl Corporation - Baton Rouge, Louisiana
May 25, 1973 to November 1, 1973
Container Dump at Site B
Permit # 730D009

Description of Material	Average Concentration (wt/wt%)	Kg. Dumped/ month[1]
Metallic Sodium	60	8.2×10^4
Metallic Calcium	13	1.8×10^4
Calcium Oxide	4	5.5×10^3
Sodium Oxide	13	1.8×10^4
Inert Salts	10	1.4×10^4

A maximum of 700 barrels may be dumped per month.

[1] Assumed average density of material was 1.5 g/cc.

G.A.F. Corporation, Texas City, Texas
May 18, 1973 to November 1, 1973
Direct Discharge at Site A
Permit # 730D007

Description of Material	Average Concentration (wt/wt%)	Kg. Dumped/ month[1]
2,5 - dichlorobenzoic acid (Na salt)	0.2	3.3×10^4
2,5 - dichloro - 6 nitro-benzoic acid (Na salt)	6.0	9.8×10^5
3,4 - dichloro - 6 - nitro-benzoic acid (Na salt)		
2,3 - dichloro - 6 - nitro-benzoic acid (Na salt)	0.7	1.1×10^5
2,5 - dichloro - 4 - nitro-benzoic acid (Na salt)	0.8	1.3×10^5

(continued)

TABLE 5-10

G.A.F. Corporation (continued)

2,5 - dichloro - 3 - nitro-benzoic acid (Na salt)	0.3	4.9×10^4

A maximum of 18,000 tons are permitted to be dumped during permit.

[1] Calculated from maximum permitted tonnage and 1 ton = 907 kg.

E.I. DuPont - Beaumont, Texas
May 1, 1973 to November 1, 1973
Direct Discharge at Site A
Permit # 730D002

Description of Material[1]	Average Concentration (wt/wt%)[2]	Kg. Dumped/ month[3]
Acrylonitrile	0.005	1.1×10^3 kg.
Acetonitrile	0.01	2.2×10^3 kg.
Heavy Nitriles	0.4	8.8×10^4 kg.
HCN		6.6×10^3 kg.
Sulfate as $(NH_4)_2SO_4$	4.7	1.0×10^6 kg.
Methanol	1.6	3.5×10^5 kg.
Propanol	1.6	3.5×10^5 kg.
Iso-butanol	1.6	3.5×10^5 kg.
Dinitrophinol	0.01	2.2×10^3 kg.
Benzene	0.06	1.3×10^4 kg.
Dinitrobenzene	0.001	2.2×10^2 kg.
Nitrobenzene	0.01	2.2×10^3 kg.
Aniline	0.01	2.2×10^3 kg.
Chromium	0.03 ppm.	0.66 kg.
Copper	0.21 ppm	4.4 kg.
Lead	<0.01 ppm	<0.22 kg.
Mercury	<0.001 ppm	<0.02 kg.

(continued)

TABLE 5-10

E.I. DuPont - Beaumont, Texas (continued)

Zinc	0.22 ppm	4.8 kg.
Cadmium	<0.01 ppm	<0.22 kg.

Specific gravity - 1,020 (average)

[1] Not to exceed 24,000 tons per month

[2] Data from permit

[3] Calculated for maximum amount allowed, from data presented in this table. 1 ton (short) = 907 kg.

E.I. DuPont - La Porte Texas
May 1, 1973 to November 1, 1973
Direct Discharge at Site A
Permit # 730D004

Description of Material	Average Concentration (wt/wt%)	Kg. Dumped/ month[1]
Inert Salts	4.3	1.3×10^6
Methylene Chloride	0.1	3.2×10^4
Formaldehyde	0.1	3.2×10^4
Other Organics (Thiuram-compounds)	1.0	3.2×10^5

Specific gravity - 1.01 (average)

Maximum of 35,000 tons are permitted to be dumped during permit

[1] Calculated from maximum quantity disposed and 1 ton = 907 kg.

(continued)

TABLE 5-10 (continued)

E.I. DuPont - LaPlace, Louisiana
May 22, 1973 to November 1, 1973 (5.4 months)
Container Discharge at Site B
Permit # 730D005

Waste Code Number[1]	Approximate Composition	Kg. Dumped/ month[2]
1*	80-90% Dichorobutene 20% max. Organic High Boilers 1-1.5% CuCl 1.5-3% Quaternary Ammonium Salts	1.0 x 10^5
2	90-100% Carbonaceous Solids 10% max. Dichlorobutene	6.3 x 10^3
3	Mixture - High boiler tars, carbonaceous solids, and dichlorobutene	1.26 x 10^3
4*	20% - NaCl Brine 30% - Organic Amines 35% - Chloroprene Dimers 10% - Chloroprene & Dichlorobutene high polymers 5% - Phenothiazince and Paratertiary butyl catechol residues	6.3 x 10^4
5	Chloroprene polymers	1.0 x 10^3
6	90% - Carbonaceous Solids 10% - Aqueous HCl	2.0 x 10^3
7 & 8	Essentially all cyanoprene polymer with residual quantities of NaCn	2.0 x 10^3
9	Carbonaceous solidys slurry in water - traces of organics	4.0 x 10^3
10	Variable - NaCl brine, benzene, dicyanobutene, traces of cyanide and copper	1.0 x 10^3
11	Carbon solids	3.1 x 10^2

(continued)

TABLE 5-10

E.I. DuPont - LaPlace, Louisiana (continued)

12*	65% - NaCl brine 20% - Carbonaceous and Polymeric organic solids 15% - Filter aid and Diatomaceous earth precoat 100 ppm cu. 200 ppm (CN)	2.4×10^5
13	Inert shell and dirt	2.0×10^4
15	Polystyrene Ion exchange resin pellets	8.3×10^2
17	Inert shell and dirt	4.0×10^3
18	HCl solution	4.0×10^3
19	Carbonaceous solids	4.0×10^3

* To be discontinued November 1, 1973

[1] From permit

[2] Calculated from length of permit and amounts permitted for discharge

---

E.I. DuPont - Belle, West Virginia
May 1, 1973 to November 1, 1973
Direct Discharge at Site A
Permit # 730D006

Description of Material	Average Composition (wt/wt%)	Kg. Dumped/ month[1]
Sodium Terephthalate	7	4.8×10^5
Ethylene Glycol	7	4.8×10^5
Sodium Styrene Sulfonate	1	6.8×10^4
Antimony	1300 ppm	8.9×10^3
Mercury	12 ppb	0.8

(continued)

TABLE 5-10

E.I. DuPont - Belle, West Virginia (continued)

Arsenic	8.7 ppm	5.9 x 10
Zinc	5.7 ppm	
Manganese	11.6 ppm	8.1 x 10
Iron	29.5 ppm	2.0×10^2

A maximum of 7,500 tons may be disposed during permit.

Specific gravity - 1.08 average

[1] Calculated from maximum quantity permitted to be dumped and 1 ton = 907 kg.

Shell Chemical Company - Deer Park, Texas
November 1, 1973
Direct Discharge at Site A
Permit # 730D008A

Description of Material	Average Composition (wt/wt%)	Kg. Dumped/ month[1]
Trichloropropane	22	3.7×10^5
Tetrachloropropyl ether	8	1.4×10^5
Dichloroethane	10	1.7×10^5
Trichloroethane	25	4.2×10^5
Dichlorobutance	30	5.1×10^5
Other:	5	8.5×10^4
Dichloropropene		
Dichloropropane		
Allyl Chloride		
Dichlorohydrin		
Glycerine		
Tetrachloroethane		

(continued)

TABLE 5-10

Shell Chemical Company - Deer Park, Texas (continued)

Trichloroethylene

Tetrachloroethylene

A maximum of 32,000 barrels (42 gallons) are permitted to be dumped per month. Total Shell waste is 205,000 barrels. Of this amount, 55,000 barrels or 27% is chloronated hydrocarbons.

[1] Calculated by assuming 27% of maximum monthly discharge was chloronated hydrocarbons. Specific gravity = 1.10 - 1.35, 1.23 avg.

The deep water circulation pattern of the western Gulf of Mexico is unknown but has been shown (Leipper *et al.* 1972) to be greatly influenced by ring currents which break from the loop current and move westward. It is impossible to estimate either the direction or current speed at Dump Site B because the ring currents are a random phenomenon which can influence the water column to a depth of 10^3 meters.

Mathews *et al.* (1973) proposed a circulation model based on ^{14}C for the western Gulf of Mexico. Their data suggest that the lateral transport of intermediate water (400 to 800 meters) from east to west is a means of renewing western Gulf intermediate water. The deep waters of the western Gulf appear to be renewed by downward migration of intermediate water caused by eddy diffusion. The residence times for these water masses have been postulated to be 120 years and 270 years, respectively.

Within the Gulf of Mexico, the continental shelf ranges in width from 20 miles off the Mississippi delta to more than 100 miles off the Texas coast. Although the average slope of the area near Site A is slightly less than 1° (Shepard 1963), Gealy (1955) has described it as "hummocky". Direct shear test results, coupled with the infinite slope theory, indicate that the marine sediments of this area would be stable to great thicknesses even on steep slopes (Morelock 1969).

In the area of Disposal Site B, there is a trough-like valley which does not approach the coast. The topography of this area is highly irregular and subject to landslides due to the dynamic instability of the sediments.

Davies and Moore (1970) identified three distinct sediment sources from their study of mineral assemblages in the Gulf of Mexico. These are the Mississippi, the Rio Grande, and the rivers of northeastern Mexico. In annual discharge, the Mississippi River (516.0 x 10^6 tons/year) has been estimated to completely overshadow its nearest competitor, the Rio Grande (19 x 10^6 tons/year). The sedimentation rate at Dump Site B has been estimated by Huang and Goodell (1970) to be 30 cm per 10^3 years.

South and west of the Sabine River the influence of the Mississippi is reduced as a result of dilution by sediment derived from the major Texas rivers (Brazos, Colorado, Sabine, and Trinity). Dump Site A is located in this area, and the rate of sedimentation in this section has been estimated by Watson and Angino (1969) to be 3.4 cm per 10^3 years.

The fauna are semi-tropical, and the species of both invertebrates and fish are numerous and diverse. Fishing in the Gulf harvests over 60 species of fish and 20 species of invertebrates. Shrimp is the predominant commercial fishery product. The shrimp fishery operates across the entire continental shelf, but it is concentrated in the shallower nearshore waters. During 1967-1968 the most valuable of the fish were menhaden; snappers; mullets; mixed groundfish species used for animal feed; weakfish; and groupers in decreasing order. Oysters and crabs are the important shellfish products (Ketchum 1972). Sports fisheries are important in the area.

In the 1960's, the total Gulf fisheries production was approximately 28 percent of the United States' total production. Between Pascagoula, Mississippi and Port Arthur, Texas, 21 percent of the country's total fishery production was landed. This region has been called the Fertile Fisheries Crescent by Gunter (1967) (Figure 5-6) and reflects the proximity of the largest estuarine region in North America. Dump Site B lies on the periphery of the Crescent.

In the Gulf of Mexico, two disposal methods are used. The first method involves the discharge of wastes through a submerged pipe into the turbulent wake of a barge. This technique is employed at Dump Site A. Site B, off the Louisiana coast, is used exclusively for materials which

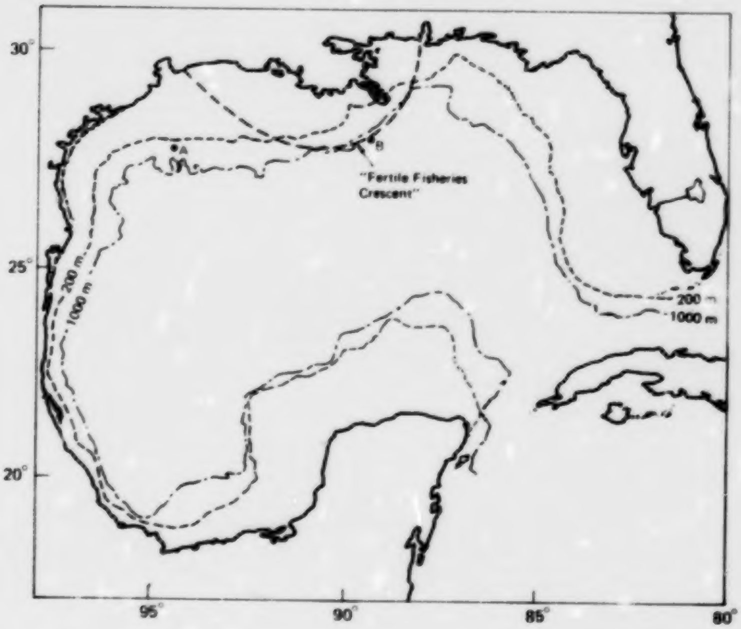

30°
25°
20°
A
B
"Fertile Fisheries Crescent"
200 m
1000 m
200 m
1000 m
95°
90°
85°
80°

FIGURE 5-6

Gulf of Mexico

are placed in barrels before discharge. Two companies use this site for disposal.

The Shell Chemical Company at Deer Park, Texas, discharges a two-phase system of liquid wastes (Shell Chemical Co. 1973). The top or aqueous phase consisted primarily of chlorinated hydrocarbons. Toxicity information indicated the threshold toxicity for the waste as 10^{-3} percent of saturation (Shell Chemical Co. 1973). Based on a solubility of 1.9 x 10^{-4} gm/ml for trichloropropane in seawater the resultant threshold toxicity would be 1.9 x 10^{-3} mg/l.

Wastes from duPont facilities at La Porte and Beaumont, Texas, and Belle, West Virginia were discharged at Site A, but now go to Site B. The La Porte plant wastes consist of inert salts, light organics, and organic residues from fungicide production. The Beaumont plant wastes consist of organic and inorganic chemicals from one process, and the Belle plant wastes contain both inorganic and organic materials. The Beaumont and Belle wastes do not have pesticide or herbicide components.

We were unable to obtain toxicity information on the duPont wastes. Submission of these values to EPA is expected. The Beaumont waste includes components with toxicity values from less than 1 mg/l to over 10^5 mg/l. The La Place, Louisiana plant discharges a wide variety of inorganic salts, industrial organics and chlorinated hydrocarbons in 55-gallon drums at Site B. We were unable to locate information on the toxicity of these components.

The General Aniline and Film Corporation at Texas City, Texas, discharges a mixture of chlorinated nitrobenzoic acid compounds resulting from the preparation of a pre-emergent soy bean herbicide. Bioassay results provided for an EPA report show 96-hour TLm values of 1.5 percent for Pompano, 1.0 percent for Brown Shrimp, 2.1 percent for the dinoflagellate *G. halli* and 0.26 percent for the diatom *C. nana* (Ball *et al.* 1974). These values are based on relative percentage of discharged material.

The Ethyl Corporation in Baton Rouge, Louisiana, discharges barrels of calcium and sodium metals and salts and other inert salts. We found no toxicity information for these wastes.

SOUTHERN CALIFORNIA BIGHT

The Southern California Bight is essentially the continental margin off one of the largest population centers of the United States. It is an open embayment extending roughly from Point Conception, California to Cabo Colnett, Mexico (Figure 5-7), with its oceanward boundary at approximately the 10^3 meter contour. The geography, sources of contaminants, and the physical and chemical characteristics of the bight have been extensively reviewed by the Southern California Coastal Water Research Project (SCCWRP) in a three-year study (SCCWRP 1973) and are therefore treated only briefly here.

The topography of the Southern California Bight consists of a smooth, narrow continental shelf, a narrow slope, a wide continental borderland, and a true continental slope (Figure 5-7). The area has many faults and as many as 32 submarine canyons. The borderland area is a rough region of basins and troughs interrupted by ridges and eight offshore islands. The submarine canyons tend to guide material from land into the offshore sediments. They do not penetrate the true continental slope.

The circulation pattern, in general, is southward along the edges of the Bight and northward through the offshore islands (Figure 5-8). There should be a net loss of water to the south. The patterns vary seasonally, with eddies common in summer and autumn. Circulation patterns near land are greatly affected by winds and bottom topography. We found little information on bottom currents in this area. It is an area of upwelling with large volumes of the deep water coming to the surface, often at the heads of the submarine canyons.

The principal water characteristics affecting the organisms of the Southern California Bight are temperature, salinity, and concentrations of dissolved oxygen. Upwelling is especially significant in controlling the plankton base of the marine food chain in the Bight, and nitrogen is the limiting nutrient. Fluctuations in temperature, salinity, dissolved oxygen, or nutrient concentrations are rapidly reflected in the plankton.

There are three principal benthic faunas in the Southern California Bight: the soft-bottom shelf community, the basin fauna, and those organisms living in

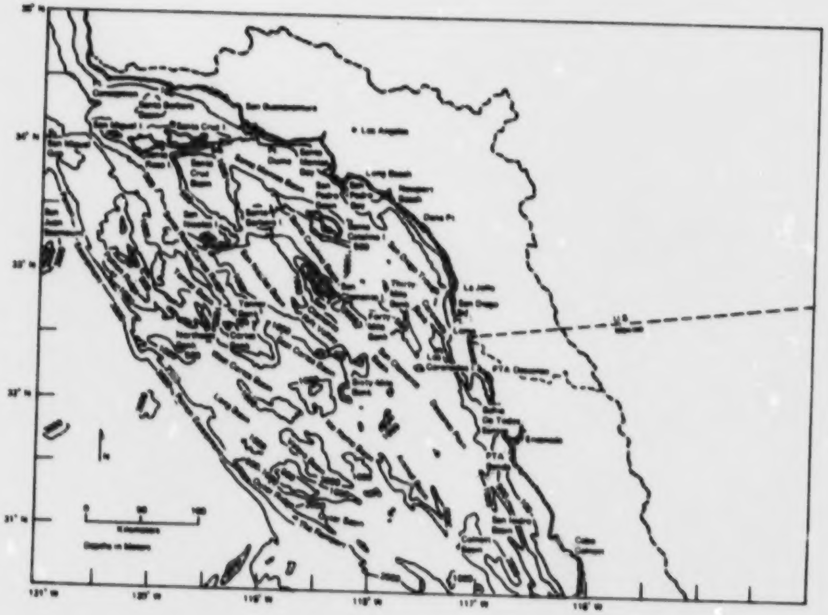
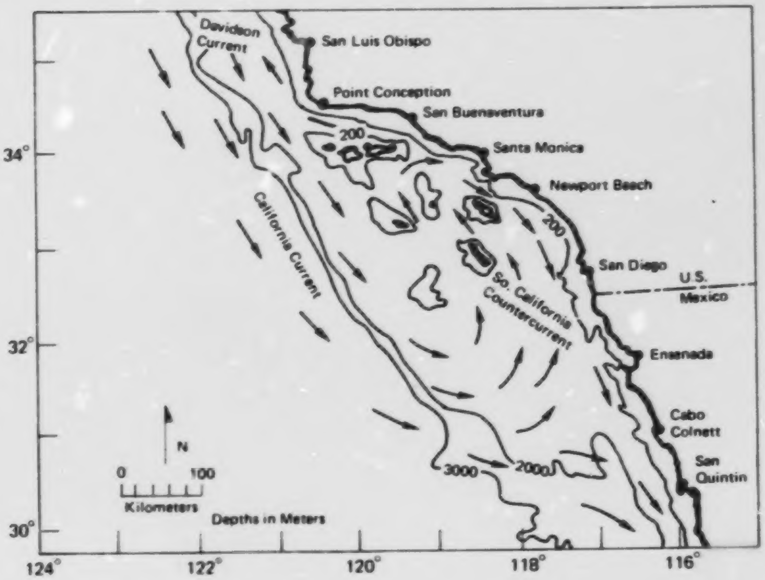

Los Angeles
Long Beach
Dana Pt
La Jolla
San Diego
U.S.
Mexico
Ensenada
34° N
33° N
32° N
31° N
121° W
120° W
119° W
118° W
117° W
116° W
0
50
100
Kilometers
Depths in Meters

FIGURE 5-7

Source: SCCWRP 1973

The Sea Floor of the Southern California Bight the submarine canyons. The basin fauna is less diverse and lower in species density and total biomass than the shelf community. Fauna in the canyons is generally intermediate between that of the shelf and the basins, it is subject to large fluctuations, and the fauna of each canyon is relatively isolated.


Davidson Current
San Luis Obispo
Point Conception
San Buenaventura
Santa Monica
Newport Beach
200
200
California Current
San Diego
U.S.
Mexico
So. California Countercurrent
Ensenada
Cabo Colnett
San Quintin
N
0
100
Kilometers
Depths in Meters
3000
2000
34°
32°
30°
124°
122°
120°
118°
116°

Source: SCCWRP 1973

FIGURE 5-8

Mean Geostrophic Flow at 200 m Depth in the Southern California Bight (Arrows Show Direction and Magnitude of Flow)

Commercial fisheries in the California region land approximately 1.5 x 10^5 tons each year. A large, active sportfishing community catches an equivalent amount.

Some unexploited or moderately exploited resources, especially pelagic fish still exist in this region. Catches could conceivably increase substantially especially if some of these pelagic resources were to be more fully exploited.

The fisheries of the Southern California Bight include many other than demersal species, principally large migratory fish. However, the demersal fish are most directly affected by the introduction of human produced materials into the area, and the various species tend to be associated in complex relationships. Species vary daily, seasonally, with temperature, upwelling, and fishing pressure.

Each year approximately 5.2 x 10^{11} kg of solid material enters the Southern California Bight from municipal waste treatment outflows (1.4 x 10^9 m^3/yr), discrete industrial sources (0.25 x 10^9 m^3/yr) and surface runoff (0.6 x 10^9 m^3/yr) (Tables 5-11, 5-12). In addition, 7.7 x 10^9 m^3 of returned cooling water and 2 x 10^{13} m^3 of advected ocean water enter the Bight area annually.

Approximately 85 percent of the municipal wastewaters of the southern California coastal basin are discharged to the ocean through outfalls (SCCWRP 1973). The remainder is reused or released at inland locations. The discharge of effluent and sludge by this mechanism results in a buildup of high levels of organic matter in the sediments in the area of the outfall. The area subject to organic loading varies with the dynamics of the surrounding water system and with the degree of waste treatment employed. Although the use of secondary treatment as required by NPDES regulations will reduce the organic loading, these procedures would not be expected to reduce the quantities of nonbiodegradable pesticides and heavy metals introduced into the coastal waters by sludge disposal.

One hundred fifty-six industries discharge wastes directly or by means of storm drains into the Los Angeles and Long Beach Harbors (Table 5-13).

TABLE 5-11

Municipal Waste Water Discharges to Southern California Coastal Waters, 1971

Discharger	Flow (m^3/day)	Type of Treatment	Ocean Outfall Length (m)	Ocean Outfall Depth (m)
Goleta San. Dist.	12,095	Primary	1,800	28
City of Santa Barbara	19,352	Primary	1,100	14
Montecita San. Dist.	1,935	Secondary	440	11
Summerland San. Dist.	242	Secondary	240	6
Carpinteria San. Dist.	3,145	Secondary	920	9
City of San Buenaventura				
Seaside Plant	6,531	Primary	800	11
Eastside Plant	9,676	Secondary		
Port Hueneme San. Dist.	8,467	Primary	1,900	18
City of Oxnard	29,028	Primary	1,750	16
City of Los Angeles				
Hyperion Plant	568,465	Primary	8,000	60
	241,900	Secondary	(effluent)	
	12,095		11,000 (sludge)	100
Los Angeles Co. San. Dist. Joint Water Pollution Control Plant	897,449	Primary	2,000	50
			2,600	65
			3,600	60
City of Los Angeles Terminal Island	19,594	Primary	730	18
City of Avalon	484	None	120	26
U.S. Navy (San Clemente Island)	242	None		
Sunset Beach San. Dist.	484	Primary	520	
Orange Co. San. Dist.				
Plant No. 1	108,855	Primary	8,300	60
	24,190	Secondary		
Plant No. 2	181,425	Primary		

(continued)

TABLE 5-11 (continued)

City of Laguna Bch.	5,564	Primary	980	25
So. Laguna Bch. San. Dist.	2,903	Secondary	520	18
Dana Point San. Dist.	5,564	Secondary	1,200	12
City of San Clemente	4,354	Secondary	210	9
City of Oceanside	9,676	Secondary Oxidation Pond		
County of San Diego Encine (Vista-Carlsbad)	11,369	Primary	5,300	30
San Elijo (Cardiff-Solana Beach)	2,661	Primary	3,700	15
City of San Diego Point Loma Plant	217,710	Primary	3,200	64
Joint International Outfall	14,514	Chlorination	43	0

Source: SCCWRP 1973

TABLE 5-12

Discrete Industrial Waste Dischargers on the Southern California Coast

			Pipe	
Discharger	Type of Waste	Flow (m^3/day)	Length (m)	Depth (m)
Phillips Petroleum Point Conception	Oil brine Tanker ballast	484		
Texaco, Inc. San Augustine	Oil brine	484		
Getty Oil, Gaviota	Oil brine Tanker ballast	387		
Shell Oil, El Capitan	Oil brine Tanker ballast	484		
Signal Oil & Gas, Ellwood	Oil brine Tanker ballast	702		
Atlantic Richfield, Coal Oil Point	Oil brine	145		
Standard Oil, Summerland	Oil brine	968		32
Standard Oil, Carpinteria	Oil brine	968	120	3
Atlantic Richfield, Rincon	Oil brine	24	76	6
Atlantic Richfield Rincon Island	Oil brine	96	800	18
Western Oil & Dev. Rincon	Oil brine	871		3
Petrol Industries Rincon	Oil brine	24		
Continental Oil, Rincon	Oil brine	1,185	150	4
Norris Oil Co. Rincon	Oil brine	120	670	3
Phillips Petroleum, La Conchita	Oil brine	871	270	6

(continued)

TABLE 5-12 (continued)

Phillips Petroleum Punta Garda	Oil brine	968	150	6
Mobil Oil, Sea Cliff	Oil brine Tanker ballast	435	950	9
Continental Oil, Pitas Point	Oil brine	653	150	4
Continental Oil, Grubb Lease	Oil brine	1,814	150	2
Getty Oil, Ventura	Oil brine Tanker ballast	144		3
Standard Oil, McGrath Beach	Oil brine	339		1
McDonnell Douglas Corp. Venice	Cooling Tower bleedoff	1,572		
Standard Oil, El Segundo	Cooling water Refinery waste	174,168	170	5
Standard Oil, Island Esther	Oil brine	2,419		
Union Oil, Platform Eva	Oil brine	48		
Signal Oil and Gas, Platform Emmy	Oil brine	194		
Signal Oil and Gas, Huntington Beach	Oil brine	1,451	300	3
Standard Oil, Huntington Beach	Oil brine	1,935	310	4
Gulf Oil, Huntington Beach	Oil line ballast	24	300	

Source: SCCWRP 1973

TABLE 5-13

Distribution of Discrete Industrial Waste Dischargers in San Pedro Bay Area

Discharge Area	Number of Discharges	Combined Flow (m^3/day)	
Los Angeles Harbor			
Outer Harbor	4	18,868	
Fish Harbor	7	4,596	
Main Channel	6	3,629	
West Basin -- Southwest Slip	15	70,635	
East Basin -- Slip 1 & 5	25	14,756	
Consolidated Slip	34	605	
Cerritos Channel	5	339	
Subtotal	96		113,428
Long Beach Harbor			
Cerritos Channel	3	27,335	
Channel Two	5	39,914	
Channel Three	7	3,629	
Southeast Basin	4	11,127	
Subtotal	19		82,005
Dominguez Channel	23		24,916
Los Angeles River Tidal Prism	3		16,933
Los Cerritos Channel	7		484
San Gabriel River Tidal Prism	8		8,708
TOTAL	156		246,474

Source: SCCWRP 1973

OVERVIEW

The discharges of dredge spoil and sewage sludge in the New York Bight have degraded the environmental quality in the area. This degradation is of local but not regional impact.

The disposal of dredge spoil will remain a problem as long as navigation of coastal and inland sea routes is maintained. The widening and deepening of existing channels will cause the volume of both virgin dredged materials and maintenance dredging spoil to increase. The concentration of contaminating substances in dredge spoil such as organic materials, heavy metals, and microorganisms should decrease as effluent control methods in the form of better sewage treatment and better industrial discharge control are realized.

The volume of sewage sludge to be disposed of can be expected to increase as higher levels of sewage treatment are reached. The impact of this higher volume of sludge will be substantial if disposed of at sea, unless sludge digestion reduces substantially the organic fraction and microorganism levels and care is taken to reduce to a minimum the heavy metal and chlorinated hydrocarbon content of the sludge. The reduction of heavy metal and chlorinated hydrocarbon content in the disposal sites will be achieved only as a result of elimination of the sources of these materials, since their removal from dredge spoil and sewage sludge is not expected to be feasible.

It can neither be demonstrated that the discharge of industrial waste chemicals to designated disposal areas using presently specified discharge methods is harmful or not harmful to the local ecosystems. The characteristics of the materials involved and the disposal sites indicate that the effects of disposal at the Puerto Rico, Gulf of Mexico chemical, and Atlantic deep-water sites may have regional as opposed to local effects. Inadequate information is available regarding the deep-water sites being used for industrial waste dumping, the history of discharge, and their nature.

Data on toxicity, bioaccumulation, biodegradability, and physical and chemical behavior of the materials and mixtures being discharged are needed.

Proper evaluation of presently discharged materials will require substantially increased effort to evaluate social and economic factors of product need, ultimate treatment or disposal methods, and the effect of the waste components on the marine system.

Wastes disposed by ocean outfalls in Southern California have had a harmful impact in the local ecosystem, but no widespread impact is evident. As concluded with regard to the New York Bight, the reduction of heavy metal and pesticide content in the disposal site areas will be achieved only as a result of eliminating the sources of these materials, since their removal from dredge spoil and sewage sludge is not expected to be feasible.

Specific recommendations are included in Chapter 1.

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Region II. 26 Federal Plaza, Room 908, New York, New York 10007, Gerald M. Hansler, Regional Administrator.

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CHAPTER 6

METALLIC WASTES

Workshop Panel

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Background Paper

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INTRODUCTION

Metal compounds comprise a major fraction of the earth's crust and are transported to the oceans by rivers, glaciers, and winds. This transport has persisted through geologic time, and we assume that the seawater system presently is in a steady state as a consequence of the distribution and disposal of crustal material. In this chapter, we address the alteration of the steady state of the ocean by the introduction of metal ions and compounds resulting from human activities.

Human activities can introduce these materials to the oceans by several transport mechanisms. Winds carry solids across coast lines. Such solids may subsequently reach the ocean surface by gravitational settling, vertical mixing, or with precipitation. Liquid industrial and municipal wastes containing metal compounds may be discharged through outfalls directly to the oceans or into rivers that ultimately discharge into the sea. River discharges may also include inadvertent contamination such as the acid drainages from abandoned coal mines and tailings.

In addition, some metallic wastes are hauled out to sea and dumped directly into offshore waters (see Chapter 5).

The steady expansion of industry, especially that defined as heavy industry, on a global scale, provides a growing potential source of metallic emissions which could reach the world's oceans. Fossil fuel combustion is a major source of a variety of airborne contaminants, including a number of metal compounds, that will continue to expand. Major industries that release metallic compounds into the atmosphere include cement, iron and steel, smelting, and petroleum refining.

River disposal may, in many cases, be considered in the same category as oceanic disposal since river water generally enters the ocean. It is hoped, however, that the increasing enforcement of water quality standards in freshwater streams and lakes of the U.S. and other highly industrialized countries will limit the impact of upstream pollutant discharges on the ocean.

Ocean disposal of wastes has played a useful role in the development of our technology because it was convenient, and in most cases economical. With careful management, there seems to be no reason why the ocean cannot continue to play a useful role in waste disposal without deleterious effects on the ocean or its total value to humanity. The ocean already contains variable amounts of the metallic compounds likely to occur in many wastes.

The toxicity levels for metallic compounds to marine organisms are in general not clearly defined. Major differences in sensitivity among organisms exist, but our present knowledge can be utilized to begin a toxicity assessment of potential hazard to the oceans (National Academy of Sciences, hereinafter referred to as NAS, 1974).

Ketchum (in press) has proposed a Relative Critical Index, which is derived by dividing the annual amount of a substance mobilized by human activities by the concentration considered to pose minimal deleterious effect. The Relative Critical Index helps to identify elements of present and future concern as pollutants of the marine environment. Analysis and recommendations concerning effects levels for metals in the marine environment may be found in *Water Quality Criteria* (NAS, 1974).

We selected iron and copper for this study because of their high mobilization by man. Iron is a major element of the earth's surface and is relatively nontoxic to organisms. Copper is not as abundant in the crust. Major urban and industrial sources of copper include combustion of fossil fuels and the primary and secondary copper industries. In the marine environment, at levels elevated over normal ones, copper is relatively toxic to organisms. Our analyses of these two elements may serve as models for the study of other elements.

IRON

General Properties

Iron comprises approximately 5.6 percent of the earth's crust, where it is the fourth most abundant element. It is essential to all organisms and is the most important of the biological trace elements (Bowen 1966). Iron is important in photosynthesis, it has been implicated in nitrogen fixation and heme synthesis, and various iron porphyrins occur in the blood of many invertebrates and mammals.

Iron concentrations in organisms range from 3500 μg/g dry tissue for plankton to 30 μg/g dry tissue for fish and 130 μg/g for crustaceans. Concentration factors of iron for phytoplankton and plankton are about 3 to 5 x 10^4 (NAS 1971).

Most of the work concerning the toxicity of iron has been with aerosol forms and with humans (Sullivan 1969). Inhalation of iron and iron dusts cause siderosis, a benign pneumonoconiosis or fibrous hardening, and iron pigmentation of the lungs. Chronic exposure may lead to bronchitis and emphysema. A possible carcinogenic role of iron oxide aerosols has been disputed due to the typical association of these oxides with other carcinogens and other pollutants such as SO_2.

Because of its importance in biochemical systems, its great abundance, its function as a nutrient, and its low toxicity, iron has not been extensively examined as a possible pollutant. However, acid-mine drainage, and its possible effects on fish in the Appalachian region, has led to investigations of both acute and chronic toxicity of iron. Iron has been identified as a nutrient which potentially limits the production of phytoplankton in the ocean (Ryther and Guillard 1959, Menzel and Ryther 1961, Ryther and Kramer 1961, Johnson 1964, Davies 1970). It is therefore possible that some addition of iron into marine systems could even be beneficial.

Atmospheric Levels

Because iron is found in high concentrations in soils, the dispersal of dust into the atmosphere results in the transport of significant amounts of the element as a part of natural dust transport. Robinson and Robbins (1971) arrived at a total natural atmospheric particulate burden of 10 μg/m^3 over oceanic areas and 20 μg/m^3 over continental areas. They estimate that soil dust comprises about 10 percent of the natural aerosols, and iron would be a natural part of this fraction.

Hoffman *et al.* (1972) analyzed over 200 atmospheric particulate samples from the windward coast of Hawaii. The average total aerosol concentration was about 12 μg/m^3. Approximately 2 percent of the particulate matter was continental dust. The iron concentration of the samples was 12 ± 9 ng/m^3. Duce (unpublished data) has found that iron concentrations over the open North Atlantic Ocean range between 10 to 15 ng/m^3. Some extreme values occurred when the Atlantic easterlies contained Sahara dust. At these times, iron concentrations up to 2.3 μg/m^3 were measured. For our analysis, we assume 10 ng/m^3 to be a reasonable concentration estimate for iron in the atmosphere of oceanic areas.

The atmospheres of continental areas are probably more variable, but an average natural particulate burden of 20 μg/m^3 of which 10 to 15 percent is continental dust is reasonable. Assuming a 5 percent Fe content, an average continental iron concentration in the troposphere would be between 100 to 150 ng/m^3.

These marine and continental values together extrapolate to an average global iron burden of about 45 ng/m^3 in the mixed layer of the atmosphere (0.5 to 1.5 km).

Freshwater Levels

Gibbs (1973), in a study of the chemistry of the Amazon and Yukon rivers, points out that only a small fraction of the total iron transported is in solution or sorbed on solids such that it is available for use in the marine environment (Table 6-1). Nearly 90 percent of the iron present is either in suspended solids or sorbed to solid phases. The Amazon, with one-fifth of the world's discharge of freshwater to the oceans, has an average dissolved iron concentration of about 30 μg/l. Gibbs recalculated the transport of Fe to the oceans in various phases, using data from Livingstone (1963) (Table 6-2). Of the total transport of approximately 10^{12} kg/yr of iron to the oceans, only 0.1 percent is in solution (Gibbs 1973).

TABLE 6-1

Iron Transport by the Amazon and Yukon Rivers

Mechanism	Amazon River (Percent of Total)*	Yukon River (Percent of Total)*
In solution and organic complexes	0.7	0.05
Adsorbed	0.02	0.01
Precipitated and coprecipitated	47.2	40.6
In organic solids	6.5	11.0
In crystalline sediments	45.5	48.2

*May not total 100 percent due to rounding off of values.

Source: Gibbs 1973.

TABLE 6-2

Annual Freshwater Discharges of Iron to the World's Oceans

Mechanism	Discharge (10^9 kg/yr)
In solution and organic complexes	1.4
Adsorbed	.09
Precipitated or coprecipitated	470
In organic solids	98
In crystalline sediments	520
Approximately	1,100

Source: Gibbs 1973, pers. comm.

By dividing the values in Table 6-2 by 34 x 10^{15} l/yr, the flow of river waters to the ocean from Livingstone (1963) and Alekin and Brazhnikova (1961), an average value for the natural iron concentration in various phases for the world's rivers can be obtained. Based on these data, we have used an average dissolved iron concentration of 40 μg/l for the world's freshwaters.

Marine Levels

Large variations in the concentration of iron in seawater have been observed because most of it is in particulate forms which are inhomogeneously distributed. Measurements by Lewis and Goldberg (1954) showed an average dissolved iron concentration of 3.4 μg/l for seawater.

Microgram concentrations of dissolved iron in seawater are supported by more recent GEOSECS data (Spencer *et al.* 1970). The concentration of dissolved iron in seawater is probably controlled by complexing of Fe with ligands. In the pH range of seawater, most of the iron is probably present as either $Fe(OH)_3^0$ or $Fe(OH)_2^+$ (Byrne 1974).

Sources Of Iron To The Environment

Table 6-3 summarizes fluxes and levels of iron in the environment. The following discussion examines these releases and some environmental consequences, and identifies areas where we lack the knowledge to assess potential impact on the environment.

Atmosphere

Robinson and Robbins (1971) estimate that the annual global pollution particulate emissions between 1966 and 1968 averaged about 92 x 10^9 kg/yr. Of this 44 x 10^9 kg, or nearly 50 percent, came from the coal industry. Of the three types of coal (bituminous, anthracite, and lignite), bituminous and lignite are grouped together for statistical summaries and account for over 90 percent of coal produced.

The emissions from a coal-fired steam plant are extremely variable and are determined by coal processing, boiler types, and efficiency of emission controls. Shannon *et al.* (1968) estimated that 100 tons of coal produce one ton of particulate emissions. The chemical composition of these emissions depends on the specific coal and its impurities. Bolton *et al.* (1973), in doing a mass balance on a generating plant with modern emission controls, also found a great deal of variation in emissions and estimated an average iron content of about 10 percent.

Noncoke production in U.S. industry (e.g., industrial boilers) consumes about 20 percent of the coal produced. Robinson and Robbins (1971) estimated a particulate emission factor of 2.6 percent for this consumption, based on studies performed by Vandegrift (1970).

Coke production in industry consumes about 20 percent of all the coal used in the U.S. Particulate emissions from coke production are not generally available. For the purpose of our analysis, Robinson and Robbins' (1971)

TABLE 6-3

Fluxes and Levels of Iron in the Environment (Units are 10^9 kg/yr unless otherwise Indicated)

Receiving Reservoir	Source				Natural Concentration Level
	Natural		Man-Mobilized		
	Dissolved	Particulate	Dissolved	Particulate	
Atmosphere	NA	12	NA	8.5	45 ng/m^3 - global avg. 10 ng/m^5 - oceans alone
Oceans	1.4	1.1×10^3	1.0	2.3	3.0 μg/l (Diss.) 0.1 μg/l (Part.)
Freshwaters	NA	NA	5.0	?	30 μg/l (Diss.) -30 mg/l (Part.)
Undifferentiated Aquatic	NA	NA	0.1	1.0	-

factor of 0.3 percent is used. Emissions from the remaining types of coal consumption probably amount to between 0.2 and 1.0 percent. This remaining consumption is primarily for power generation.

Based on these estimates, approximately one percent of all the coal consumed on a global basis is released to the atmosphere as particles less than 2 microns in size and containing about 10 percent iron. Using a global consumption of bituminous and lignite coal of about 2.9 x 10^{12} kg/yr, an annual emission of 2.9 x 10^{9} kg Fe/yr is calculated.

Demand for coal along with other fossil fuels will probably continue to expand for some time. Table 6-4 lists production figures for bituminous coal and lignite as well as forecasted demands for the year 2000. These forecasts are based on average annual growth of GNP, population growth, and energy demands, and include allowances for synthetic gas and liquid fuel production and the growth of other energy sources (for a thorough analysis, see U.S. Bureau of Mines, 1970). According to these estimates, by the year 2000, the United States will be consuming 40 percent of the world's soft coal production, assuming production equals consumption. Of this estimated U.S. demand, nearly 90 percent will arise from the electric power industry.

Particulate emissions from petroleum combustion, refining, and natural gas combustion amount to an estimated 2 x 10^{9} kg/yr (Robinson and Robbins 1971), or approximately 0.1 percent of the annual consumption of these materials (2 x 10^{12} kg/yr). The average iron content of oil is estimated to be 2.5 x 10^{-6} g/g (Bertine and Goldberg 1971). Assuming no emission controls on these sources, there is a potential emission of iron of approximately 5 x 10^{6} kg/yr from petroleum combustion, which is small compared with the coal combustion source of 2.9 x 10^{9} kg/yr.

Iron and Steel Production The production of iron and steel is the largest estimated source of atmospheric iron aerosols other than natural soil. For 1968, emissions of fine particles from the various production sources resulted in a total estimated U.S. release to the atmosphere of 7 x 10^{10} kg Fe per year. Table 6-5 shows the breakdown of releases from individual processes for the

1968 U.S. production of 1.19 x 10^{11} kg. Two processes, materials handling and steel furnace operations, account for nearly all emissions.

TABLE 6-4

Production and Estimated Demand of Bituminous Coal and Lignite

Year	Production (10^9 kg) U.S.	Production (10^9 kg) Rest of the World	Demand (10^9 kg) U.S.	Demand (10^9 kg) Rest of the World
1968	496	-	454	-
1969	510	-	462	-
1970	548	-	469	-
1971	502	2,328	462	-
1972^e	537	2,375	1,780	2,600
2000^e	-	-	1,150-2,370 (1,800)	2,070-3,060 (2,600)

e = estimated

Source: U.S. Bureau of Mines 1970, Commodity Data Summaries.

The U.S. produces about one-fifth of the world's total of pig iron and raw steel (Table 6-6). Because of the concern over air pollution in the United States and a probable greater application of air pollution control technology than other nations, we extrapolated U.S. emissions to the globe as a lower limit for releases. By applying the U.S. emissions factor of 6 x 10^{-3} to the 1972 global steel production, we estimate the release of Fe to the atmosphere on a world basis to be 3.7 x 10^9 kg/yr from the iron and steel industry.

TABLE 6-5

Particulate Emissions from the Iron and Steel Industry (1968)

Source	Annual Handling (10^9 kg)	Emission Factor (kg/10^3 kg)	Net Control Factor	Annual Emissions (10^9 kg)	Percent Iron	Iron Emitted (10^9 kg)
Ore crushing	75 ore	0.9	0	0.07	(70)	0.05
Materials handling	119 steel	4.5	0.32	0.36	(63)	0.23
Pellet plants	?	?	?	0.07	(63)	0.04
Sinter plants	46 sinter	19	0.90	0.09	33	0.03
Blast furnaces	81 iron	59	0.99	0.05	50	0.03
Foundry operations[1]	16 metal	7.2	0.27	0.08	(63)	0.05
Steel furnaces						
Open hearth	60 steel	11	0.40	0.40	55	0.22

TABLE 6-5 (continued)

Steel furnaces (cont)						
Basic oxygen	44 steel	18	0.99	0.01	54	<0.01
Electric arc	15 steel	9	0.78	0.03	29	0.01
Scarfing	119 steel	1.3	0.68	0.05	(63)	0.03

Total Emissions: 1.21×10^9 kg particulates; 0.70×10^9 kg iron.

Steel Production: 1.13×10^9 kg/119×10^9 kg steel.

[1] Foundries .08 x 10^9 kg/16×10^9 kg metal.

( ): Estimated from iron content of ores and ferric oxide content of other steelmaking dusts (Shannon *et al.* 1971).

TABLE 6-6

World Pig Iron and Raw Steel Production (Units: 10^9 kg)

Nation	Pig Iron 1971	Pig Iron 1972e	Raw Steel 1971	Raw Steel 1972e
United States	74	82	110	120
France	18	19	23	24
West Germany	30	33	40	44
Japan	73	76	89	94
United Kingdom	15	16	24	26
Other Free World	78	82	111	115
Communist Countries (except Yugoslavia)	143	150	187	195
WORLD TOTAL	431	458	584	618

e = estimated

Source: U.S. Bureau of Mines 1972.

Forecast demands for iron in the United States in the year 2000 average approximately 1.4 x 10^{11} kg, corresponding to an annual growth of 1.7 percent. Estimated demands for the rest of the world average approximately 5.9 x 10^{11} kg, or an annual average growth rate of 2 percent per year (U.S. Bureau of Mines 1970).

Cement Industry The raw materials used in the making of cement contain iron compounds; and during the manufacturing process, some of the compounds are lost to the atmosphere, with estimated emission factors between 85 and

105 kg/ton. Table 6-7 gives domestic and world cement production for 1971 and 1972. Portland cement accounts for nearly 95 percent of the total U.S. production (U.S. Bureau of Mines 1973). Table 6-8 summarizes emissions of particles less than 2 microns in size from the cement industry in the U.S. The iron emission factor for U.S. cement production is 6 x 10^{-4} per production unit. The U.S. produces approximately one-eighth of the world's cement (U.S. Bureau of Mines 1973). On the basis of Table 6-6 and the U.S. emission factor, we estimated an annual emission of 3.8 x 10^{8} kg Fe as fine particles from the world's cement industry.

TABLE 6-7

World Cement Production (Units: 10^9 kg)

Year	U.S.	Non-U.S.	World Total
1971	73	519	592
1972^{e}	77	560	637

e = estimated

Source: U.S. Bureau of Mines 1973.

Stone, Sand, and Gravel The crushed stone industry produced an estimated 4 x 10^{12} kg of crushed stone in 1972 (U.S. Bureau of Mines 1973). Of this, approximately 9 x 10^{10} kg were produced in the U.S. Vandegrift *et al.* (1971) give an emissions factor in the U.S. of 8.6 kg particulates per 10^3 kg and a net control factor of 0.2 for these emissions. Using a crustal abundance of 5.6 percent for Fe and extrapolating U.S. emissions, we estimated a global emission of Fe from crushed stone processing to be (4 x 10^{12} kg/yr) (8.6 kg part./10^3 kg) (0.8) (0.056 kg Fe/kg part.) = 1.5 x 10^9 kg Fe/yr.

TABLE 6-8

Particulate Emissions from the U.S. Cement Industry (1968)

Source	Handling (10^9 kg)	Emission Factor (kg/10^3 kg)	Net Control Factor	Annual Emissions (10^9 kg)	Percent Iron[1]	Iron Emitted (10^9 kg)
Wet Process	40					
Kilns		75	0.88	0.36	6.0	0.022
Grinders, Dryers, etc.		11	0.88	0.05	3.5	0.002
Dry Process	28					
Kilns		75	0.88	0.25	6.0	0.015
Grinders, Dryers, etc.		30	0.88	0.10	3.5	0.004
Total	68			0.76		0.043

[1] Derived from Shannon *et al.* (1970) and Goldberg 1973, pers. comm.

Source: Vandegrift *et al.* 1971.

Municipal Waste Incineration Robinson and Robbins (1971) estimate that 4 x 10^9 kg particles are emitted on a global scale from general incineration operations. Since most of this material is nonmetallic and does not have significant contributions of rock, it probably adds very little to an atmospheric inventory at particulate Fe. We estimate a maximum of 1 percent of the ash from municipal incineration to be Fe. This would amount to 4 x 10^7 kg Fe/yr, which is small when compared with the other sources of iron.

Summary of Atmospheric Iron Inventory Table 6-9 summarizes major sources of iron to the atmosphere. Using annual crustal weathering estimate of 2 x 10^{11} kg and a crustal abundance for iron of 5.6 percent, 1.2 x 10^{10} kg/yr of Fe are mobilized. The one area in Table 6-9 that we are not presently able to approximate is the area where humans serve as a weathering mechanism through such activities as highway construction, clearing operations, mining operations, and agricultural practices. These could be relatively small sources as far as transport to the oceans is concerned because large particles with limited airborne travel would be expected.

TABLE 6-9

Major Sources of Iron to the Atmosphere

Source	Flux (Units: 10^9 kg/yr)
Natural (Crustal Weathering)	12
Man-Induced	
Coal Consumption	2.9
Iron and Steel Industry	3.7
Cement Industry	0.4
Crushed Stone Industry	1.5
Weathering (Man-Induced)	?
TOTAL (Man-Induced)	8.5

We estimate that human activity introduces small iron particles (less than 2 μm in size) to the atmosphere in amounts approximately two-thirds of those introduced by natural crustal weathering (Table 6-9).

Marine and Freshwaters

Titanium Dioxide (TiO_2) Industry This industry, with almost 2 x 10^6 tons of product per year, produces iron containing wastes which are frequently disposed of at sea. Ninety-nine percent of the TiO_2 produced is used as pigment. The two principal ore sources are ilmenite and rutile; and both contain iron, the former in large amounts. Ilmenite is the source of about 85 percent of the world's titanium. The TiO_2 composition of ilmenite ranges between 37 and 65 percent. The remainder consists of iron oxides except for approximately 2 to 8 percent of other metal oxides and silica. Titanium dioxide is produced commercially by sulfate and chloride processes, both of which produce acid-iron wastes if ilmenite is used. The sulfate process produces more waste per ton of product than the chloride process.

In the sulfate process, ilmenite or titanium slag (titanium slag is produced in Canada from ilmenite for export and contains 71 percent TiO_2 and FeO equivalent to about 16 percent Fe_2O_3) is dissolved with sulfuric acid. Iron metal scrap or other reductants breakdown any oxidized iron to the ferrous state. Part of the iron is then precipitated as hydrated iron sulfate. While some of the iron sulfate may be recovered, most of it is discarded together with the acid wastes from the further processing of the TiO_2. The resulting waste has a pH less than 0.1 and an iron concentration of 40 to 60 g/l in addition to other dissolved trace metals.

Compilation of a materials flow for the world's titanium dioxide industry is not possible because some required information is proprietary and thus not available. However, the U.S. Bureau of Mines estimates worldwide TiO_2 production to be 1.6 x 10^6 tons. (Wessel 1973, pers. comm.) (Table 6-10).

One U.S. producer of TiO_2 disposes of acid-iron wastes by deep wells, and thus iron from its wastes does not reach the oceans. Some producers use rutile (low-iron

TABLE 6-10

World Titanium Pigment Capacity in 1972 (Units: 10^6 kg)

Nation	SO_4 = process	Cl^- process
United States[e]	380	360
Australia	25	9
Canada	52	-
Brazil	4.2	-
Belgium	15	-
Finland[a]	23	-
India	8.5	-
Japan[b]	93	-
South Africa	10	-
France	88	-
Germany, West[e]	200	-
Italy[c,d]	46	-
Netherlands	18	-
Norway	20	-
Portugal	15	-
Spain	14	-
Poland[e]	(32)	-
Mexico	11	-
United Kingdom[e]	200	64
Total*	~1,220	~430

[a] May be as high as 36.

[b] One company manufacturing artificial rutile, some Cl- capacity.

[c] May be as high as 64.

[d] May not have been operational in 1972.

[e] Estimated.

*Not including Poland.

Source: Wessel 1973, pers. comm.

ore), resulting in little iron discharged to the environment. Some production is at inland sites and, while river discharge of iron occurs, we cannot estimate what amount reaches the oceans.

If, however, all of the wastes produced by the world's TiO_2 industry reached the sea, and all were produced from ilmenite, we estimate that the maximum possible annual iron input to the oceans would be:

$$(1.65 \times 10^9 \text{ kg } TiO_2 \text{ produced/yr}) \left(Fe / TiO_2 \right) \text{ ore ratio.}$$

where Fe = average ilmenite iron content = 35 percent,

TiO_2 in average world ore used = 55 percent.

Thus, the maximum iron release equals $(1.65 \times 10^9)(35/55) = 10^9$ kg/yr. This amount would be less than 0.1 percent of the total iron discharged by the world's rivers (Table 6-2).

Aluminum Industry The aluminum industry produces extensive iron wastes in the conversion of bauxite to alumina in the form of red muds. Red muds contain about 20 percent solids (0.5 to 2 microns), with their chemical composition dependent on the type of ore used and the conversion process (Fursman *et al.* 1970).

In the U.S., approximately 6.4×10^9 kg of red mud solids (dry weight) were produced in 1972 (estimated from data supplied by Fursman *et al.* 1970 and Stamper 1973, pers. comm.). Assuming that the iron content of dry red mud averages 26 percent, there were approximately 1.7×10^9 kg of iron involved.

Most red mud is impounded in lagoons. However, about 20 percent of the U.S. production may be discharged to the aquatic environment. If this 20 percent of the muds produced by alumina processing in the U.S. were released to the aquatic environment (marine and freshwater), they would contain approximately 3×10^{10} kg Fe/yr. Thus, red mud does not appear to be a problem in terms of iron releases in the U.S., even with an annual projected growth rate of over 7 percent.

The estimated 1972 U.S. and world aluminum productions are 3.7×10^9 kg and 11×10^9 kg, respectively (U.S. Bureau of Mines 1973). Using this ratio, we extrapolated U.S. data to a potential global release of 5.7×10^9 kg

Fe/yr from alumina production. The amount actually released to the environment cannot be estimated accurately. If it is 20 percent, as assumed for the U.S., the annual release would be about 10^9 kg Fe/yr in particles less than 2 microns.

Sewage Effluents Sewage outfalls in the U.S. are now coming under a permit system administered by the U.S. Environmental Protection Agency, but as yet, sufficient data on these effluents are not available (Chapter 5). In the Southern California region, which contains about eleven million people, approximately 4 x 10^9 liters per day of sewage effluents are discharged to the Pacific by outfalls (Southern California Coastal Water Research Project, hereinafter referred to as SCCWRP, 1973). Using an average dissolved iron content of 1 mg/l for these effluents, an annual discharge of 1.5 x 10^6 kg Fe/yr is estimated for approximately 5 percent of the U.S. population. By extrapolation, the U.S. release of dissolved Fe would be 3 x 10^{11} kg/yr to both freshwater and marine environments. Lack of world data on the extent of sewage treatment facilities prevents us from developing a more complete analysis of these releases, but the possible impact seems minor.

Data are not available to assess possible releases of iron from raw sewage, but judging from the treated effluents discussed above, the potential impact seems insignificant.

Atmospheric Fallout The atmospheric transport of iron concludes with the removal of aerosols into the oceans through precipitation, vertical transport, or gravitational settling. Atmospheric iron concentrations over the world's oceans average 10 ng/m^3 (Robinson and Robbins 1971). If the dry fallout is calculated from this value, using the deposition velocity concept (Chamberlain 1960), a deposition rate of 0.1 ng/m^2/sec is derived for a deposition velocity of 1 cm/sec. For the world's oceans (3.6 x 10^{14} m^2), an annual dry deposition of 1.1 x 10^9 kg results. A ratio of about 1:5 is often used to relate dry deposition to total deposition including rainfall (Junge 1963). There results then a value of 5.5 x 10^9 kg for the annual atmospheric deposition of iron to the oceans.

This estimate includes both man-influenced and natural processes. The ratio of these two fluxes, obtained from our estimates of global emission rates, is 12 x 10^{12} : 8.5 x 10^{12} or 1.4:1 for natural versus human emissions (Table 6-3). Thus, the oceans receive an estimated 2.3 x 10^9 kg of iron from human emissions and 3.2 x 10^9 kg from natural sources. It should be emphasized that this is an estimated global average value and specific areas can be expected to vary significantly, especially in the mid-latitudes of the northern hemisphere.

Acid-Mine Drainage Acid-mine drainage results from the oxidation of pyrite yielding ferrous sulfate and sulfuric acid. Most of the iron released is initially $FeSO_4$ which oxidizes to $Fe_2(SO_4)_3$ and then hydrolyzes to $Fe(OH)_3$ in the environment. Assessing the degree to which mining has contributed to acid-mine drainage is difficult because it is a natural occurrence once used to detect coal seams. We will assume that 95 percent is due to human activities. This value may not be far from correct since about 60 percent of the drainage in Appalachia comes from abandoned mines.

The U.S. Environmental Protection Agency's Region III Wheeling Field Office has analyzed the actual discharges from over 5,000 acid-mine sources located in roughly 10 percent of the 3.2 x 10^5 km^2 Appalachian region affected by acid-mine drainage (McPhilliamy 1973 pers. comm.). Mine drainage is extremely variable, and only single samples were taken from discharge sites during a single inventory. The total iron discharge amounted to 2.6 x 10^5 kg/day or 9.5 x 10^7 kg/yr for the region or 9.5 x 10^8 kg/yr extrapolated to the total discharge in Appalachia.

In 1971, the Appalachian region produced approximately 75 percent of the total U.S. coal production (McPhilliamy 1973, pers. comm.). The Appalachian region encompasses most of the abandoned mines in the U.S., which contribute to the greatest input of mine drainage. Mines in the western United States are relatively recent producers of coal and for lack of rain probably do not produce as much as 25 percent of the acid drainage in the U.S. A reasonable release for the annual acid-mine drainage in the U.S. is 10^9 kg/yr Fe. Globally, approximately 5 x 10^9 kg/yr may be released.

Iron and Steel Industry Insufficient data are presently available to assess the impact of this industry on the iron introduced to the oceans directly or through rivers.

Fallout of Atmospheric Particulate Iron The input of naturally-weathered material and industrial emissions to freshwater surfaces and eventual transfer to the ocean are probably negligible when compared to other sources, and will be disregarded.

Summary of Aquatic Iron Inventory Table 6-11 summarizes the fluxes of iron to the aquatic environment. Iron fluxes to the oceans are dominated by particulate materials carried by rivers.

COPPER

General Properties

Copper is one of the first elements mined by man, having been sought even in prehistoric times. Although native (or elemental) deposits of copper have been found, it most commonly occurs in a variety of minerals as compounds of sulfides, oxides, and carbonates. Copper comprises approximately 5 x 10^{-3} percent of the earth's crust.

Copper, like iron, is very important in biological systems. Bowen (1972) indicates that more than 30 proteins and enzymes have been found to contain copper. Copper concentrations in organisms have an approximate range of 2 μg/g dry tissue for mammals to 50 μg/g dry tissue for some crustaceans (Bowen 1966).

Certain organisms are very sensitive to low levels of copper in the environment, and copper and its salts have been used as pesticides to remove algae from ponds and extensively in antifouling paints which release to the water.

Hoffman *et al.* (1972) found copper concentrations in the Hawaiian marine atmosphere of 2 ± 2 ng/m^3. Duce (1973, pers. comm.) found copper in the North Atlantic westerlies of 3.5 ng/m^3 and in the North Atlantic easterlies (in Sahara Dust at times) as high as 15 ng/m^3. Higher values than these have been reported; however, their validity may be questionable due to possible contamination of samples from brush wear on high-volume sampler motors (Hoffman and Duce 1971). Recent improvements in sampling techniques and analysis indicate that even the 2 ng/m^3 Cu for

TABLE 6-11

Fluxes of Iron to Marine and Freshwaters[1]
(Units: 10^9 kg Fe/yr)

	Marine Environment	
Source	Dissolved	Particulate
Natural		
River runoff	1.4	1,100
Atmospheric fallout	NA	3.2
TOTAL	1.4	1,103.2
Man-induced		
TiO_2 industry	1.0	0.0
Atmospheric fallout	NA	2.3
TOTAL	1.0	2.3
Marine and Freshwater Environments (undifferentiated)		
Man-induced		
Sewage effluents	0.1	?
Aluminum industry	0.0	1.0
TOTAL	0.1	1.0
Freshwater Environments		
Man-induced		
Iron and steel industry	?	?
Acid-mine drainage	5.0	?
TOTAL	5.0	?

[1] Background: Marine: Dissolved Fe = 3.0 μg/l
Particulate Fe = 0.1 μg/l

Freshwater: Dissolved Fe = 40 μg/l
Particulate Fe = 30 mg/l

uncontaminated air may be an order of magnitude or more too high (Duce 1973, pers. comm.). In view of these improvements in analytical techniques, we believe that an average natural background burden of copper in the marine atmosphere of 0.2 ng/m^3 is a reasonable estimate. Over rural land areas, EPA high-volume sampler network data indicated that Cu concentrations were in the range of 10 to 20 ng/m^3 (National Air Pollution Control Administration (NAPCA) 1968). These data could again represent contamination from brush wear.

If we assume that the only natural source of copper to the atmosphere is crustal weathering, a natural introduction of Cu to the atmosphere can be calculated. Multiplying the amount of continental dust entering the atmosphere, 200 x 10^9 kg annually (Robinson and Robbins 1971), by the crustal abundance of copper of 55 x 10^{-6} g Cu/g and assuming a 4-day residence time and a uniform global distribution lead us to an estimated atmospheric Cu concentration of 0.02 ng/m^3, considerably lower than the marine concentrations mentioned above.

Freshwater Concentrations

Copper can, in principle, complex strongly with organic ligands (Stumm and Morgan 1970); however, satisfactory assessments of the degree of organic complexing in natural waters have not been made. Morel and Morgan (1972) have included the effects of some organic ligands in their numerical model of speciation in an aqueous system.

Table 6-12 gives the associations of copper with various phases in the Amazon and Yukon rivers (Gibbs 1973). Based on this analysis, Gibbs (1973, pers. comm.) has calculated the total input of copper to the oceans, using Livingstone's (1963) discharge data (Table 6-13). In this compilation, Gibbs uses an average dissolved Cu concentration of approximately 2 μg/l.

Marine Chemistry

The concentrations of dissolved copper reported in seawater range over more than one order of magnitude. A concentration of 1 μg/l (3 x 10^{-8}M) is a commonly accepted

TABLE 6-12

Copper Transport in the Amazon and Yukon Rivers

Mechanism	Amazon River (Percent of Total)	Yukon River (Percent of Total)
In solution and organic complexes	6.9	3.3
Adsorbed	4.9	2.3
Precipitated and coprecipitated	8.1	3.8
In organic solids	5.8	3.3
In crystalline sediments	74.3	87.3

Source: Gibbs 1973.

TABLE 6-13

Annual Discharge of Copper to the World's Ocean

Mechanism	Discharge (10^7 kg/yr)
In solution and organic complexes	6.1
Adsorbed	22
Precipitated or coprecipitated	36
In organic solids	28
In crystalline sediments	540
Approximately	630

Source: Gibbs 1973, pers. comm.

level. Solubility considerations (Kester 1972, Krauskopf 1956) indicate that if the solubility of copper in seawater is set by malachite, the concentration of Cu should be about 5×10^{-6}M. Since it is two orders of magnitude less, malachite solubility is not the controlling factor (Kester 1972).

The chemical forms that dissolved copper may take in seawater have been assessed by Kester (1972) and Zirino and Yamamoto (1973). Both approaches indicate that copper exists as an uncharged species in seawater ($CuCO_3°$ and $Cu(OH)_2°$). These treatments do not consider organic complexes.

Sources of Copper in the Environment

Table 6-14 summarizes fluxes and levels of copper in the environment. The following discussion examines these releases and some environmental consequences, and identifies areas where we lack the necessary knowledge to assess potential impact on the environment.

TABLE 6-14

Fluxes and Levels of Copper in the Environment (Units: 10^7 kg/yr Unless Otherwise Indicated)

	Source				
	Natural		Man-induced		
Receiving Reservoir	Dissolved	Particulate	Dissolved	Particulate	Natural Concentration Level
Atmosphere	NA	1.0	NA	1.6	~0.2 ng/m^3
Oceans	6	630	2.9	0	Diss. ~1µg/l
Freshwaters	0	NA	1.4	NA	Diss. ~2µg/l Part. ~180µg/l
Undifferentiated Aquatic	-	-	5.0	-	-

Atmosphere

Bertine and Goldberg (1971) give a copper concentration in coal of 15 x 10^{-6} g/g. If we assume that particulate control equipment is 90 percent effective, and an annual coal consumption of 2.9 x 10^{12} kg, an annual copper emission of 4.3 x 10^{6} kg/yr is calculated. Bertine and Goldberg (1971) give an annual emission of approximately 2 x 10^{7} kg Cu/yr from petroleum combustion.

Copper Industry

The copper industry is, most likely, the largest single source of copper-containing solid wastes. Table 6-15 is derived, in part, from Shannon *et al.* (1968) and is a compilation of the estimated particulate emissions from the copper industry in the United States. The ore-crushing process is the largest single industrial source and contributes about 25 percent of the total copper emissions. These are probably relatively large particles with somewhat limited transport potential. The secondary copper industry accounts for about 22 percent of the estimated emissions.

Table 6-16 gives estimates for 1972 world mine production of copper. The United States produces approximately 25 percent of the world's copper. The projected annual growth rate of copper demand is about 4 percent for the U.S. and 4.5 percent for the world (U.S. Bureau of Mines 1970).

The total atmospheric copper emissions from the U.S. industry amounts to approximately 2.9 x 10^{6} kg/yr (Table 6-15). Multiplying by 4 for a world estimate (Table 6-16) yields 1.2 x 10^{7} kg/yr.

Summary of Atmospheric Copper Inventory

Table 6-17 summarizes major sources of copper to the atmosphere.

TABLE 6-15

Particulate Emissions from the Copper Industry, U.S.

Source	Annual Handling (10^9 kg)	Emission Factor (kg/10^3 kg)	Net Control Factor	Annual Emissions (10^6 kg)	Percent Cu	Cu Emitted (10^6 kg)
Primary						
Ore Crushing	153 (ore)	0.9	0	140	(0.5)	0.70
Materials handling	1.3 (Cu)	4.5	0.32	4.0	(2)	0.08
Roasting	0.5 (Cu)	76	0.85	5.7	9	0.51
Reverberatory furnace	1.3 (Cu)	94	0.81	23	3	0.69
Converters	1.3 (Cu)	107	0.81	26	1	0.26
					TOTAL	2.24
Secondary						
Material preparation						
wire burning	0.3 (insulated wire)	125	0	38	(1)	0.38
sweating furnaces	0.06 (scrap)	6.8	0.19	0.3	(1)	0.01

(Continued)

TABLE 6-15 (continued)

blast furnaces	0.3 (scrap)	23	0.68	2.2	4	0.09
Smelting and refining	1.1 (scrap)	32	0.57	15	(1)	0.15
					TOTAL	0.63
					TOTAL Cu EMITTED	2.87

TOTAL EMISSIONS: 2.54 x 10^8 kg/yr U.S. (<2 μm); 2.9 x 10^6 kg Cu/yr.

Note: Numbers in Parentheses are Estimates.

Source: Shannon *et al.* 1968; Davis 1972.

TABLE 6-16

World Mine Production of Copper (Given as Cu) for 1972

Nation	Production (10^9 kg)
United States	1.5
Canada	0.7
Chile	0.7
Peru	0.2
Zaire	0.4
Zambia	0.8
Other Free World	1.2
Communist Countries (except Yugoslavia)	1.0
TOTAL	6.5

Source: U.S. Bureau of Mines 1973.

TABLE 6-17

Major Sources of Copper to the Atmosphere

Source	Flux (10^6 kg/yr)
Natural (Crustal Weathering Only)	10
Man-Induced	
Coal Combusion	4.3
Copper Industry (Primary and Secondary)	12
TOTAL MAN-INDUCED	16.3

Inputs of Copper to Marine and Freshwater

Industry There is no evidence of any large discharges of copper to the sea except for atmospheric fallout and antifouling paint. The production of soluble waste copper in the U.S. has been analyzed by Ottinger *et al.* (1973), and a general discussion of industrial pollution control may be found in Lund (1971). The major sources of soluble copper wastes are the electroplating industry, spent copper pickle liquors, the textile industry, and possibly the printed circuit and chemical industries.

Rinse waters from the electroplating of copper are alkaline solutions containing anywhere from 50 to 10^4 mg/l Cu. Losses from plating operations vary considerably with the process used, the size of the operation, and the metal plated. The average may be as high as 70 percent for the chrome industry (Lancy 1973, pers. comm.). Ottinger *et al.* (1973) and Lancy (1973, pers. comm.) indicate that between 7 and 10 percent of the copper purchased by an industry for plating purposes enters waste streams. In 1971, approximately 5.3×10^6 kg of Cu were consumed by the electroplating industry in the U.S. Using a 10 percent loss factor, this indicates a discharge of approximately 5×10^5 kg Cu.

The pickling of copper is accomplished by passing the copper through 5 to 15 percent HCl or H_2SO_4 to remove oxides. Essentially all copper produced is pickled, and the average loss in pickling is 0.1 to 0.2 percent which, with a production of 1.5×10^8 kg Cu in the U.S. in 1972, amounts to approximately 2×10^6 kg soluble copper lost annually.

The textile industry generates copper wastes in the dyeing and finishing of cloth. Aniline dyeing consumes some 8×10^4 l per 450 kg of cotton dyed, while water soluble dyes consume some 16×10^3 l per 450 kg dyed. Dyes are extremely variable, but the U.S. textile industry consumes approximately 5×10^9 liters of water per year, which may contain as much as 900 mg Cu/l. In addition, two copper compounds, copper ammonium fluoride and copper ammonium carbonate, are used in the mildew-proofing of cotton. On these bases, it has been estimated that the textile industry generates 2.7×10^6 kg of copper in its waste waters annually (Ottinger *et al.* 1973).

The amount of copper used by the chemical industry in catalyst production is not available. It has been estimated (Ottinger *et al.* 1973) that 3 x 10^5 kg of copper is generated as wastes from spent copper catalysts annually.

The printed circuit industry generates copper wastes from the etching of laminated circuit boards to remove copper that is not part of the circuit. In 1971, approximately 6.5 x 10^6 kg of Cu was consumed by this industry in the U.S. A loss rate of slightly over 3 percent or 2 x 10^5 kg has been estimated (Ottinger *et al.* 1973).

Summing the above estimates indicates that U.S. industry generates approximately 6 x 10^6 kg of soluble copper wastes which extrapolates to 2.5 x 10^7 kg Cu/yr of soluble copper waste on a global basis.

We were unable to locate estimates of the extent of controls on these wastes. It has been mentioned above that the electroplating industry figure of 5 x 10^5 kg Cu represents a loss to the environment. Based on data in Lund (1971), a figure of 50 percent control for the textile industry, which uses an alum coagulation process, appears reasonable to us. We assume a similar process and an estimate of 50 percent control for pickling. Lacking data for controls on wastes from the printed circuit industry and from chemical catalysts, we assume a zero control factor. Table 6-18 summarizes our estimates of U.S. industrial copper releases to the aquatic environment which total 3.4 x 10^6 kg/yr. Multiplying this value by a factor of 4 yields a global estimate of approximately 1.4 x 10^7 kg Cu/yr.

Data on the flux of copper in mining waste drainage streams were not available.

Sewage Effluents Data on sewage outfalls in the Southern California region indicates that 5.9 x 10^5 kg Cu/yr. are discharged in the area by municipal outfalls (SCCWRP 1973). Extrapolating these data to a U.S. estimate, on the basis that 5 percent of the U.S. population lives in the Southern California area, yields 1.2 x 10^7 kg Cu/yr of Fe discharged in domestic sewage to both fresh and marine environments. Extrapolating further to a world estimate yields 5 x 10^7 kg Cu/yr. Data to assess the validity of this extrapolation are not available.

TABLE 6-18

Estimated U.S. Industrial Copper Releases to the Aquatic Environment

Source	Copper Released (10^6 kg)
Electroplating	0.5
Pickling of Copper	1.0
Textile	1.4
Printed Circuit	0.2
Spent Copper Catalysts	0.3
TOTAL	3.4

Atmospheric Fallout Using the approach discussed previously for fallout of iron, we estimated copper deposition to the oceans. The deposition velocity for copper, 0.07 cm/sec (Pierson *et al.* 1973) is significantly less than the 1 cm/sec value used for iron. The resultant dry deposition estimate is 1.6×10^6 kg/yr, which results in a value of 8×10^6 kg Cu/yr for total oceanic fallout.

Antifouling Paints Because of its biocidal properties, copper is a component in antifouling marine finishes. SCCWRP (1973) estimates that 3.2×10^5 liters of paint containing about 3.6×10^5 kg of copper are used annually to protect boats in the Southern California Bight region. It is our estimate that about 60 percent of this copper leaches into the ocean during the use of the boat. This amounts to an input of approximately 2.2×10^5 kg/yr of copper.

The Southern California Bight area contains about 3 percent of the marine recreational boats in the U.S. (Chapter 3) (SCCWRP 1973). Based on this estimate, the annual input of dissolved copper to the ocean, but especially to the bays, harbors, and estuaries, from antifouling paints in the U.S. is about 7×10^6 kg/yr. Multiplying this by 3 for a world estimate yields 2.1×10^7 kg/yr. Antifouling paints are probably not extensively used in freshwaters and are not considered here as a source of copper in freshwaters. In addition, particulate copper, contained in paint flakes resulting from surface preparation during repainting, may also enter the water. What happens to this particulate copper, probably CuO, in the sediments is not known, nor is it known what amount moves into the water column. We have not included values for particles and flakes from antifouling paint in the summary of copper fluxes.

Summary of Aquatic Copper Inventory Table 6-19 summarizes the fluxes of copper to the aquatic environment.

OVERVIEW

We estimated iron and copper inputs to the oceanic environment from natural and human sources. Natural processes are dominated by river inputs, especially for particulate forms. Several human processes impact on the ocean, but coal combustion, because metals present in the fuel are partially released in fly ash, was one of the more important factors in both the iron and copper models. Because coal contains a very wide variety of trace metals, it is possible that coal combustion and fly ash emissions would be significant sources for many airborne metals.

Both iron and copper had specific industrial sources. In the case of iron, they included the heavy industrial manufacturing processes of the iron and steel industry and TiO_2 manufacturing processes, where iron in the original ores becomes a waste product. For copper, the major industrial source was the smelting industry. In the development of other models, industrial sources of other metals can probably be discovered through a review of basic metallurgical processes.

Atmospheric transport from land to ocean has not been modelled in detail. Our procedure of using the deposition velocity concept and an estimate of the oceanic background in concentration seems to provide reasonable values. However, this method does not provide estimates of deposition gradients across ocean areas. Atmospheric fallout may produce substantial changes in surface water concentrations in areas downwind of major sources.

TABLE 6-19

Fluxes of Copper to Marine and Freshwaters[1]
(Units: 10^7 kg Cu/yr)

	Marine Environment	
Source	Dissolved	Particulate
Natural		
River runoff	6	630
Atmospheric fallout	?	0.5
Man-induced		
Atmospheric fallout	?	0.3
Antifouling paints	2.1	0
TOTAL	~8	~631
	Marine and Freshwater Environments (undifferentiated)	
Man-induced		
Sewage effluents	5.0	?
TOTAL	5.0	?
	Freshwater Environments	
Man-induced		
Copper consuming industries	0.8	?
Textile industry	0.6	?
TOTAL	1.4	?

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[1] Background: Marine: Dissolved Cu ≅ 1 μg/l

Freshwater: Dissolved Cu ≅ 2 μg/l
Particulate Cu ≅ 184 μg/l

The iron and copper models indicate that these metallic elements being disposed of in ocean areas at present levels will probably result in small overall concentration changes. At present, our data on oceanic concentration patterns are not sufficient to establish the natural variability or the degree of perturbation that would cause an adverse biological effect. There may be significant impacts when relatively large injections of toxic metals to small zones such as estuaries are involved.

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CHAPTER 7

MEDICINAL WASTES

Workshop Panel

J. Goldsmith, Chairman
N. Andersen
L. Hearn
D. Wilson
J. Hedgpeth
D. Passino
F. Viets

Background Paper

L. Hearn
D. Passino
D. Wilson

Medicinal wastes result from the diagnosis, treatment, or prevention of human or animal disease. Although hospitals and clinics are obvious sources of these wastes, they are by no means the only ones.

We selected two examples, tetracycline drugs (antibiotics) and 99^{m} technetium (a radioisotope) to illustrate our strategies for evaluating the potential of medicinal wastes as marine contaminants.

TETRACYCLINES

Introduction

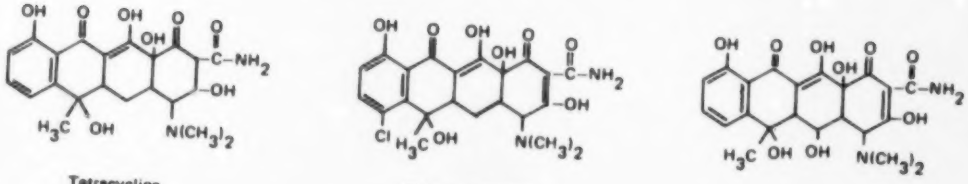
Tetracyclines are widely used in medicine and agriculture as broad-spectrum antibiotics against some gram-positive and gram-negative bacteria, rickettsia, some protozoans, actinomycetes, and larger viruses. Tetracycline is 4-(dimethylamino)-1,4,4a,5,5a,6,11,12a-octahydro-3,6,10,12,12a-pentahydroxy-6-methyl-1, 11-dioxo-2-naphthacenecarboxamide. Common tetracyclines marketed in the United States are chlortetracycline, oxytetracycline, and tetracycline. Other less-used tetracyclines are demeclocycline, doxycycline, methacycline, and minocycline.

Chlortetracycline was first marketed by Lederle Laboratories under the trade name Aureomycin in 1948 (Blackwood 1969). Chlortetracycline and oxytetracycline are used primarily in veterinary medicine; tetracycline is primarily used for treatment of humans.

The tetracyclines are yellow, odorless, crystalline solids with a slight bitter taste. The structures of the three tetracyclines which we are considering are shown in Figure 7-1. They are all derivatives of perhydronaphthacene carboxamide and are amphoteric, slightly soluble in water at pH 7, and form water soluble sodium salts and hydrochlorides. Their dry crystalline bases and their hydrochlorides are stable indefinitely, but their aqueous solutions lose activity at varying rates, which are accelerated by high pH and temperature (Figures 7-2, 7-3, and 7-4). Refrigeration increases the stability of neutral solutions of all three compounds, particularly tetracycline, which retains appreciable activity for at least 3 weeks at 4 C (Weinstein 1970). At pH 5.2 and 37 C, tetracycline retains 100 percent of its activity for at least 144 hours (English *et al.* 1953-54). All three tetracyclines isomerize spontaneously in solution to an equilibrium mixture of the original compound with its 4-epimer, which is called a quatrimycin. The quatrimycins exhibit negligible *in vitro* antibiotic activity, but they all possess broad *in vivo* antimicrobial activity which has been demonstrated in animal studies (Doerschuk *et al.* 1955).

The acid salts of the tetracyclines are soluble in alcohols and ketones, but insoluble in less polar solvents (Table 7-1).

All tetracyclines contain numerous potential sites for chelation with metal ions, and they form stable complexes with divalent and trivalent cations. The chelating ability of the tetracyclines is believed to be the source


OH
O
OH
OH
O
O
C–NH₂
OH
H₃C OH
N(CH₃)₂
Cl
OH
N(CH₃)₂

Tetracycline Chlortetracycline Oxytetracycline

(Available from several sources - xeroxed from Weinstein 1970; carbon numbering and ring labeling system is that of Kirk-Othmer, 1963-1971, Encyl. of Chem. Technol.).

FIGURE 7-1

Structural Formulas of the Major Tetracycline Antibiotics

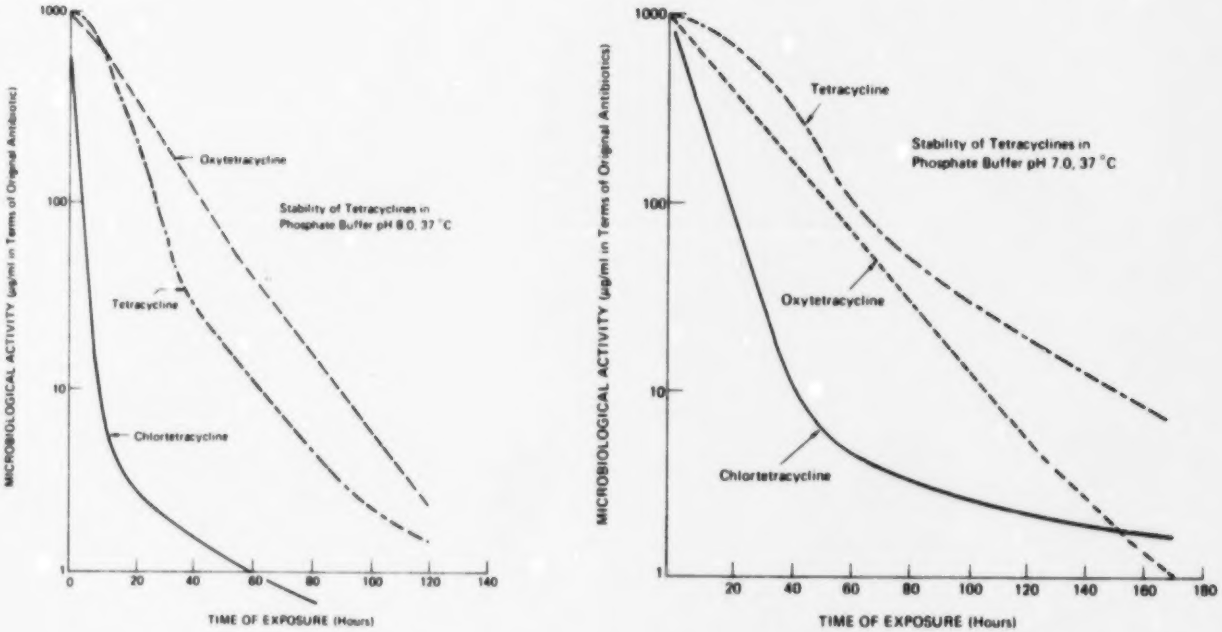
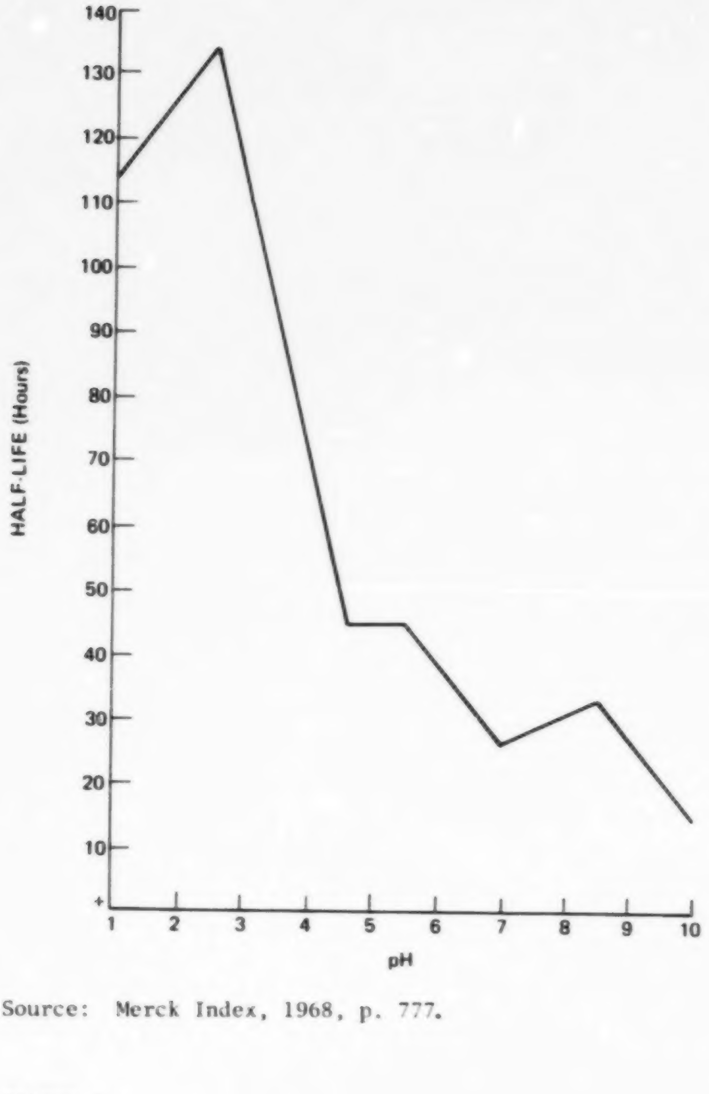


FIGURE 7-2 AND 7-3

Tetracycline Stability

Source: Bohonos *et al.* 1954.



Source: Merck Index, 1968, p. 777.

FIGURE 7-4

Decline of Half-Life of Oxytetracycline with pH in Solution at 37°C

TABLE 7-1

Solubilities of Tetracyclines at 28°C (mg/ml)

Antibiotic	H_2O	Ethanol	Benzene	Pet. Ether	CCl_4	Ethyl Acetate	Acetone	Ether	Ethylene glycol	Pyridine
Tetracycline	1.7	>20	1.05	0.005	0.315	17.3	17.4	3.7	>20	>20
Tetracycline HCI	10.9	7.9	0.25	0.0	0.10	0.75	0.75	0.60	17.72	>20
Oxytetracycline	0.60	8.1	0.037	0.0	0.055	0.85	1.6	0.13	20	>20
Oxytetracycline HCI	6.9	11.95	0.027	0.01	0.072	2.05	10.8	0.135	20	>20
Chlortetracycline	0.5-0.6	slightly	slightly	practically insoluble		slightly	slightly	practically insoluble		
Chlortetracycline HCI	8.6	1.7	0.09	0.005	0.132	0.35	0.12	0.085	3.0	>20

Source: Weiss *et al.* (1957) in Merck (1968).

of their antibiotic activity (Weinberg 1957), and it will probably be the most important property in determining their fate in the environment.

Tetracycline is usually marketed as the hydrochloride salt which decomposes at 214 C.

Chlortetracycline is the 7-chloroderivative of tetracycline (Figure 7-1). Chlortetracycline is biosynthesized by *Streptomyces aureofaciens*. The free base exists as golden yellow crystals which melt at 168-169 C. Chlortetracycline is soluble in weakly basic solutions (Table 7-1).

Chlortetracycline hydrochloride, the most common pharmaceutical preparation, exists as bitter yellow rhomboid crystals that decompose above 210 C (Merck Index, 1968) or 170 C (Wendlandt and Zief 1958).

Oxytetracycline is the generic name for 5-hydroxytetracycline, a product of fermentation by *Streptomyces rimosus*. The free base normally exists as the dihydrate, dull yellow, slightly bitter, needle-shaped crystals, which melt and decompose at 181 to 182 C. The hydrochloride of oxytetracycline exists as yellow platelets whose solubility in water is 6.9 mg/ml (Table 7-1).

The stability of oxytetracycline solutions declines with increasing pH at 37 C (Figure 7-4). Aqueous solutions of oxytetracycline hydrochloride are stable for at least 30 days at 25 C and pH 1.0 to 2.5. At 5 C between pH 3.0 and 9.0, no deactivation occurs in 30 days.

Production

The available data on United States production of bulk tetracyclines are shown in Table 7-2 and Figure 7-5. Finished pharmaceutical preparations and products used in pills, capsules, tablets, or other measured doses are excluded from this table. Complete production data are not available.

The geographic distribution of production sites of the tetracyclines is given in Table 7-3.

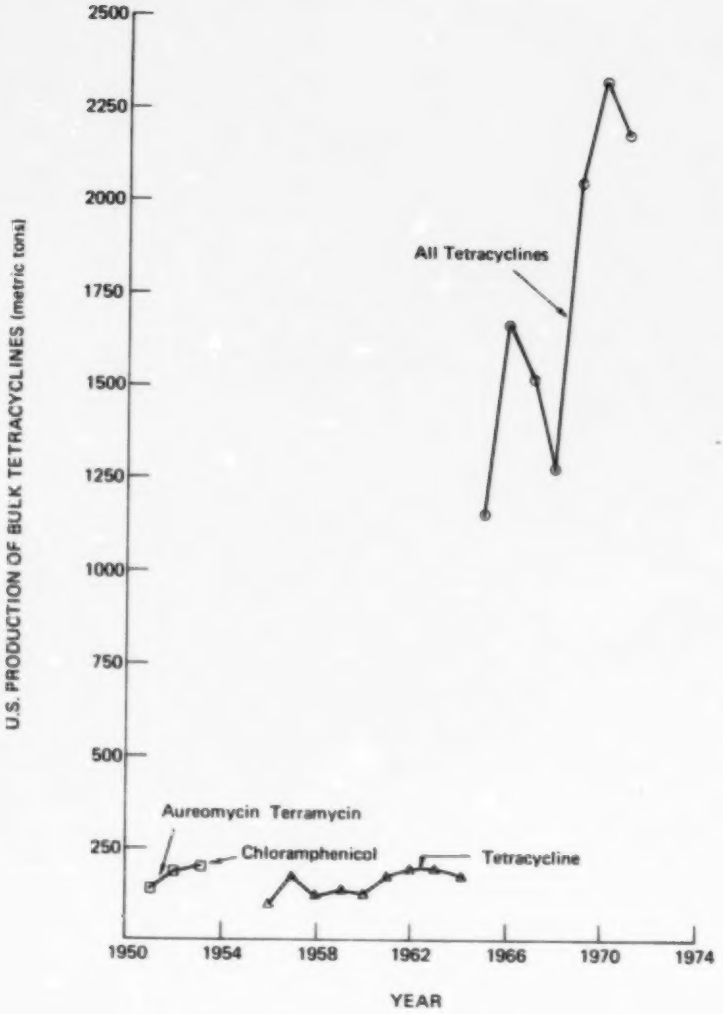
TABLE 7-2

U.S. Production of Bulk Tetracyclines

Compounds and Uses	Time Period	Production metric tons
All tetracyclines (all uses)	Jan-Apr 1973	727
"	1972	no data
"	1971	2183
"	1970	2319
"	1969	2052
"	1968	1273
"	1967	1523
"	1966	1668
"	1965	1157
Tetracycline (human and veterinary uses)	1964	176
"	1963	193
"	1962	195
"	1961	178
"	1960	130
"	1959	139
"	1958	130
"	1957	184
"	1956	100
Aureomycin[a], Terramycin[b], Chloramphenicol[c]	1953	200
"	1952	188
"	1951	140

[a] Tradename of American Cyanamid Co. for chlortetracycline
[b] Tradename of Pfizer, Inc. for oxytetracycline
[c] Not a tetracycline compound

Source: U.S. Tariff Commission. U.S. Production and Sales of Synthetic Organic Chemicals. 1951-1973.



Source: U.S. Tariff Commission 1951-1973.

FIGURE 7-5

U.S. Production of Bulk Tetracyclines

TABLE 7-3

Locations of Production of Tetracyclines

Company	Compounds	Production Site
American Cyanamid Lederle Division	tetracycline, chlortetracycline, minocycline	Pearl River, N.Y.
Bristol-Myers Co. Bristol Labs.	tetracycline	Syracuse, N.Y.
"	tetracycline	Barceloneta, P.R.
Pfizer, Inc.	tetracycline, oxytetracycline, doxytetracycline, methacycline	Groton, Conn.
Rachelle Laboratories	tetracycline, chlortetracycline, oxytetracycline	Long Beach, Calif.

Tetracyclines represent about one-fourth to one-third of all U.S.-produced bulk antibiotics by weight (Table 7-4). In 1970, 56.8 percent of all antibiotics were for medicinal use (Stanford Research Institute 1971).

The United States sales of tetracyclines are presented in Table 7-5. If we assume that the sales in 1964 and 1965 were roughly the same, and that oxytetracycline, chlortetracycline, and tetracycline comprised most of all sales, then the sales of oxytetracycline and chlortetracycline would have totaled about 300 tons. Therefore, the volume sold for veterinary medicine would have been approximately twice that sold for human medicine in 1964-1965. Because sales include exports, and because we were unable to obtain data on imports, it was not possible to equate U.S. sales with U.S. consumption. U.S. sales have fluctuated somewhat erratically in the last 6 years.

TABLE 7-4

Production of Bulk Tetracyclines Compared with Production of all Bulk Antibiotics

Year	All Antibiotics Tons	Percent Tetracyclines of all Antibiotics
1971	8140	26.8
1970	7690	30.2
1969	6000	34.2
1968	4660	27.3
1967	4300	35.4
1966	4390	38.0

Source: U.S. Tariff Commission. U.S. Production and Sales of Synthetic Organic Chemicals. 1966-1971 Preliminary.

All commercially available tetracyclines are synthesized by direct fermentation processes followed by chemical modification (Blackwood 1969).

Fermentation processes have special water and air pollution problems (Lane 1971). The fermentation waste most likely to be involved in water pollution is spent beer (Lane 1971). This spent beer is the fermented broth from which the valuable antibiotic fraction has been extracted (Lane 1971), and contains metabolites from fermentation, organic nutrients, media (Eagle and Saz 1955), and inorganic nutrients. Other liquid wastes would include solvents used to wash the mycelia before drying.

One manufacturer's waste treatment plant includes activated sludge treatment operating in parallel with a trickling filter (Lane 1971). This treatment plant is designed to reduce biochemical oxygen demand (BOD) to less than 250 ppm and suspended solids to less than 250 ppm (Manufacturing Chemists Association 1973). The effluent then enters a municipal sewage treatment plant. The effluent has not been monitored for tetracyclines (American Cyanamid Corporation 1973, pers. comm.)

TABLE 7-5

U.S. Sales (Quantity) of Bulk Tetracyclines

Compounds and Uses	Year	Sales Tons
All tetracyclines (all uses)	1971	484
"	1970	735
"	1969	381
"	1968	388
"	1967	616
"	1966	667
"	1965	472
Tetracycline (human and veterinary uses)	1964	153
"	1963	150
"	1962	131
"	1961	125
"	1960	116
"	1959	117
"	1958	110
"	1957	136
"	1956	84
Aureomycin[a], Terramycin[b], Chloramphenicol[c]	1953	161
"	1952	174
"	1951	122

[a] Tradename of American Cyanamid Co. for chlortetracycline
[b] Tradename of Pfizer, Inc. for oxytetracycline
[c] Not a tetracycline compound

Source: U.S. Tariff Commission. U.S. Production and Sales of Synthetic Organic Chemicals. 1951-1971. Preliminary.

Spent beer can be evaporated, and the resulting dry product used as an animal feed (Lane 1971). Solid wastes include the mycelia of the *Streptomyces* spp. In some cases, the mycelia are dried and used as animal feed (Forbath 1957). Otherwise, these solid wastes are dumped or used in landfill.

Human Use

Tetracycline hydrochloride is most commonly used in human therapeutics. The general route of administration is oral, but may be intravenous, intramuscular, or topical, depending on the nature and severity of the infection.

The effect of the tetracyclines is primarily bacteriostatic with bactericidal activity appearing only when the ratio of concentration of antibiotic to the initial number of cells is high. The concentration required for bactericidal effect is 8 to 10 times the minimum inhibitory concentration (Wyss *et al.* 1953). Electron microscope studies by Ruziczka and Orth (1951) have indicated that tetracyclines act primarily on rapidly growing bacteria causing pronounced morphological changes in the cells. Little change was produced in fully grown cells by contact with the antibiotic. The most widely-accepted theory concerning the mechanism of antibiotic action of the tetracyclines is that they inhibit bacterial protein synthesis.

Our understanding of the mode of action of the tetracyclines is incomplete, and the antibacterial effects of these drugs may result from a combination of activities.

Bacterial Resistance

Resistance to tetracyclines appears to result from a significant decrease in the ability of the bacteria to concentrate the antibiotic (Arima and Izaka 1963, Franklin and Godfrey 1965, Izaka and Arima 1965, DeZeeuw 1968). Sensitive bacteria actively concentrate tetracyclines so that the intracellular concentration is increased considerably above that in the medium. There is a threshold level below which the active uptake does not occur, and it is this threshold level which appears to increase. Resistant cells are capable of accumulating the antibiotic, but a much higher concentration in the medium is required before the active transport mechanism is triggered.

The antibiotic spectra of the tetracyclines are quite similar, and bacterial strains which are resistant to one of the group may be resistant to the others as well. Those differences which are observed probably result from effects of the substituents on the ability of the bacteria to absorb the antibiotic molecule.

A transferable resistance marker factor in drug-resistant strains has been demonstrated (Datta 1965, Falkow *et al.* 1966, Rownd 1966, Smith 1967, Watanabe 1967).

One undesirable side effect of tetracycline treatment is overgrowth of fungi in the gastrointestinal tract. Some preparations contain Nystatin or Amphotericin B to prevent intestinal infection by fungi, particularly *Candida albicans*.

Absorption and Excretion

Usually, the three major tetracyclines are prescribed on a schedule of one to two grams per day for adults. All of the major tetracyclines are rapidly but incompletely absorbed from the gastrointestinal tract. The presence of divalent and trivalent cations in the gut interferes with their absorption (Visconti 1971).

A considerable fraction of sorbed tetracyclines is bound to plasma proteins. Kunin *et al.* (1959) found that 47 percent of chlortetracycline, 20 percent of oxytetracycline, and 24 percent of tetracycline in the blood binds to plasma proteins. Weinstein (1970) gives ranges of 50 to 70 percent, 25 to 30 percent, and 20 to 25 percent for plasma protein binding of chlortetracycline, tetracycline, and oxytetracycline, respectively. A much higher level of plasma protein binding (69 percent) was determined by Pindell *et al.* (1959) in experiments with tetracycline in dogs. Table 7-6 gives concentrations of tetracycline HCl in serum and other body fluids after administration of the antibiotic in 500 mg doses by various routes.

Tetracyclines are reversibly bound to serum and organs but they bind irreversibly by chelation to bone, particularly in areas of active calcium apatite deposition (Buyske *et al.* 1960).

The only tetracycline which is reported to be chemically altered *in vivo* is chlortetracycline (Shirk *et al.* 1957). Kelly and Buyske (1960) concluded that tetracycline does not undergo any appreciable chemical transformation in

TABLE 7-6

Average Tetracycline Levels in Various Body Fluids Compared to Serum Levels at Time of Withdrawal of Specimen (Tetracycline HCl g/ml)

Body Fluid	Dosage	How Administered	Serum Level	Body Fluid Level
Rile	500 mg.	Intravenously, B.I.D.	6.3	66.0
Rile	500 mg.	Orally, Q.I.D.	1.5	13.0
Inflammatory peritoneal fluid	500 mg.	Intravenously, B.I.D.	4.6	10.0
Inflammatory chest fluid	500 mg.	Orally, Q.I.D.	1.8	3.9
Spinal fluid	500 mg.	Orally, Q.I.D.	5.0	1.9
Amniotic fluid	500 mg.	Intravenously, B.I.D.	4.0	5.2
Breast milk	500 mg.	Orally, Q.I.D.	2.6	1.33
Cord serum	500 mg.	Intravenously, B.I.D.	4.1	2.3
Cord serum	500 mg.	Orally, Q.I.D.	1.9	1.4
Urine	500 mg.	Intravenously, B.I.D.	4.6	125
Urine	500 mg.	Orally, Q.I.D.	2.3	110
Urine	500 mg.	Rectal suppository (single dose)	0.6	50
Urine	500 mg.	Intramuscularly (single dose)	2.0	30

Source: Maynard *et al.* 1955.

the body of the rat or the dog, and that the antibiotic is probably present in both urine and blood in chelated form with calcium.

The major route of excretion is through the kidneys, but the percent of an administered dose excreted by this means varies with the compound and route of administration. Virtually all of the tetracycline antibiotics administered to humans or animals are excreted in active form in feces and urine.

Agricultural Uses

Chlortetracycline and oxytetracycline are widely used in animal feeds. These and other antibiotics are a major factor which makes possible the mass production of livestock and poultry under crowded conditions. The tetracyclines are used primarily for two purposes: to promote growth and to improve other features such as egg production and hatchability; and to prevent and to treat diseases. Administering these drugs in the feed is more efficient than injection of individual animals.

Addition of low levels of tetracyclines to animal feeds from birth to market often results in more rapid weight gain so that the final weight of the animal at time of marketing is greater (Tables 7-7 and 7-8). For cattle on feedlots, 70 to 100 mg/animal/day has been found to give a maximum growth response.

Chlortetracycline and oxytetracycline may be administered in animal feeds as the sole antibiotic or in combination with other drugs. A complete listing of all drug combinations is found in the *Feed Additive Compendium* (Animal Health Inst. 1972).

Livestock could serve as a reservoir for resistant bacteria which could be transferred to humans (United States Department of Agriculture, Agricultural Research Service 1972).

Release to the Environment

Animals release tetracyclines in an active form in the urine and feces. Quantitative bioassays of fresh

TABLE 7-7

Indications for Use and Use Level of Chlortetracycline as an Additive in Animal Feed

Animal	Drug	Use Level	Indications for Use
chickens	chlortetracycline	10-50 g/ton	growth promotion and feed efficiency
		50-100 g/ton	prevention of chronic respiratory disease, egg production, and egg hatchability
		100-200 g/ton	treatment of chronic respiratory disease, bluecomb; prevention of synevitis
		200 g/ton	treatment of synevitis
chickens	chlortetracycline plus	10-50 g/ton	growth promotion and feed efficiency; prevention of coccidiosis caused by *E. tonella*, *E. mecratrix*, and *E. acervulina*; improving pigmentation
	Sulfanitran	0.03%	
	and Nitromide	0.025%	
	and Roxarsone	0.005%	
swine	chlortetracycline	10-50 g/ton	growth promotion and feed efficiency
		50-100 g/ton	prevention of bacterial enteritis; maintenance of weight gains in the presence of atrophic rhinitis; cervical abscesses
		100-200 g/ton	treatment of bacterial enteritis

(continued)

TABLE 7-7 (continued)

swine (continued)		200 g/ton	reduce spread of leptospirosis (feed as sole medication)
		400 g/ton	reduce shedding of leptospirae; reduce abortion rate; reduce mortality rate of newborn pigs when leptospirosis is present
	chlortetracyline plus phenothiazine	10-50 g/ton 0.3-1.0%	growth promotion and feed efficiency; aid in removing nodular worms (*Oesophagostomum*)
beef cattle and non-lactating dairy cattle	chlortetracycline	70 mg/head/day	growth promotion and feed efficiency; prevention of liver abscesses
		70 mg/head/day	cattle weighting up to 700 lb: above plus reduction of bacterial diarrhea; prevention of foot rot
		100 mg/head/day	cattle weighting over 700 lb: reduction of bacterial diarrhea; prevention of foot rot
		350 mg/head/day	cattle weighting up to 700 lb: prevention of anaplasmosis
		500 mg/head/day	cattle weighting 700-1,000 lb: prevention of anaplasmosis
		750 mg/head/day	cattle weighting 1,000-1,500 lb: prevention of anaplasmosis

Source: The Animal Health Institute 1972.

TABLE 7-8

Indications for Use and Use Levels of Oxytetracycline as an Additive in Animal Feed

Animal	Drug	Use Level	Indications for Use
catfish	oxytetracycline	2.5-3.75 g per 100 lb. of fish in ration for 10 days	control of bacterial hemorrhagic septicemia caused by *Aeromonas liquefaciens* and Pseudomonas disease
salmonids	oxytetracycline	2.5-3.75 g per 100 lb. of fish in ration for 10 days	control of ulcer disease caused by *hemophilus piscium*; furunculosis caused by *Aeromonas salmonicida*; bacterial hemorrhagic septicemin caused by *Aeromonas liquefaciens*; Pseudomonas disease
sheep	oxytetracycline	10-20 g/ton	promote growth and feed efficiency
		50 g/ton	prevention of bacterial diarrhea, lamb dysentery, and white scours of lambs
		100 g/ton	treatment of bacterial diarrhea, lamb dysentery, and white scours of lambs

(continued)

TABLE 7-8 (continued)

sheep (continued)		25 mg/head/day	reduction of losses due to enterotoxemia (overeating disease)
chickens	oxytetracycline	50 g/ton	prevention of diseases from oxytetracycline susceptible organisms during periods of stress
		5-7.5 g/ton	hatching to market to promote growth and feed efficiency
		10-50 g/ton	increase egg production
		50-100 g/ton	improve hatchability in times of stress; prevention of bluecomb
		200 g/ton	control fowl cholera during periods of outbreaks
	oxytetracycline plus	200 g/ton	prevention of fowl typhoid; nullorum and paratyphoid; aid in prevention of coccidiosis
	Furazolidone plus	0.0055%	
	Arsanilic acid	0.005-0.01%	
	oxytetracycline plus	100-200 g/ton	prevention of complicated chronic respiratory disease (air-sac infection)
	Meomycin base	35-140 g/ton	prevention of bacterial entoxisis and in the control of Neomycin-sensitive organisms associated with bluecomb

Source: The Animal Health Institute 1972 manure from cattle feedlots indicated that 75 percent of the chlortetracycline received in the feed was excreted (Elmund *et al.* 1971). The half-life of the antibiotic residue in feedlot manure was greater than 20 days at 4 and 28 C. Elmund *et al.* (1971) found 14 μg/g in "aged" manure; however, the time of aging was not stated.

From 1962 to 1970, the trend has been toward larger feedlots (National Academy of Sciences, hereinafter referred to as NAS, 1972). In 1970, there were 105 feedlots with 16,000 to 32,000 head of cattle and 41 feedlots with greater than 32,000 head. Thus, the number of large point sources for tetracyclines from manure is increasing. About 3.5 tons of Aureomycin per year are being used in some feedlots (Viets 1973, pers. comm.).

In 1970, there were 3,409 million dairy cattle, beef cattle, poultry, swine, and sheep in the U.S. (NAS 1972). The total production of wet manure from these animals was estimated to be 1,200 million tons per year for 1970 (Table 7-9).

TABLE 7-9

Estimated Production of Manure by Farm Animals in 1970 in the United States

Animal	Size kg	Wet Manure/ Animal kg/yr	Animal Population Millions	Total Wet Manure - 10^6 ton/yr
Dairy cattle	450	10,900	21	230
Beef cattle	350	7,800	91	710
Poultry	2.2	40	3,220	130
Swine	45	1,400	57	80
Sheep	45	680	20	14
TOTAL	-	-	3,409	1,164

Source: NAS 1972.

In 1970, approximately 60 percent of all antibiotics were for medicinal use (Stanford Research Institute 1971). If we estimate that total U.S. consumption is about 4 thousand tons and assume that one-half of this is for agricultural use, then total consumption by farm animals would be approximately 2 thousand tons. If 75 percent of the tetracyclines consumed are excreted in active form, then 1500 tons would be expected to be found in fresh manure.

If we assume that 10 percent of the total tetracyclines in fresh manure enter the aquatic environment in active form through surface runoff, leaching, and percolation, and that 90 percent remains on land either permanently or until deactivated, then our estimated total tetracyclines entering the aquatic environment of the U.S. from animal manure would be approximately 150 tons per year.

We were unable to find any measurements of tetracyclines from marine or freshwaters.

Fish Culture Use

Oxytetracycline is probably the most widely used antibiotic in treatment of fish diseases (Wolf and Snieszko 1964). The concentration of oxytetracycline administered in the feed is 2.5 to 3.75 grams per 100 pounds (45 kg). Oxytetracycline is also to the holding water of aquarium fishes which are being shipped or stored (Snieszko 1959).

A series of papers has been published on the uses of oxytetracyclines in fish culture. A review article by Herman (1969) included tables summarizing fish diseases for which oxytetracycline has proved an effective treatment (Tables 7-10 and 7-11).

Oxytetracycline is excreted from treated fish. It appears likely that all oxytetracycline that is consumed by fish would be excreted except for that portion which remains for longer periods (months) in the bone and scales. We were unable to find data to indicate that anyone has attempted to measure oxytetracycline in the feces of the fish. Therefore, we do not know whether oxytetracycline is excreted in active form by fish as it is by mammals.

TABLE 7-10

Infections Effectively Treated by the Addition of Oxytetracycline to the Feed

Pathogen	Species	Dosage	Reference
A. liquefaciens	Golden shiner *Notemigonus crysoleucas*	2.5 g/100 lb.	Meyer, 1964
A. salmonicida	Brook trout *Salvelinus fontinalis*	25-75 mg/kg	Snieszko, Griffin and Friddle, 1952
"	Chinook salmon *Oncorhynchus tshawytacha* Steelhead trout *Salmo gairdneri* Coho salmon *O. kisutch*	5-36 g/100 lb.	Conrad, per. comm., 1966
C. columnaris	Chinook salmon *O. tshawytacha*	2.0 g	
	Steelhead trout *S. gairdneri*	3.5 g/100 lb.	Barney, per. comm., 1966
"	Cutthroat trout *S. clarki*	3.5 g/100 lb.	Warren, per. comm., 1966
H. piscium	Brook trout *S. fontinalis*	75 mg/kg	Snieszko, Friddle, and Griffin, 1951
Pseudomonas sp.	White catfish *Ictalurus catus*	2.5 g/100 lb.	Meyer and Collar, 1964

Source: Herman 1969.

TABLE 7-11

Infections Effectively Treated by the Addition of Oxytetracycline to the Water

Disease	Species	Dosage	Reference
Fin rot	Minnow *Hybognathus* sp. Mosquitofish *Gambusia affinis* Fathead minnow *Pimephales promelas*	Not reported	Irwin, 1959
Fin rot	Bluegill *Lepomis macrochirus* Fathead minnow *P. promelas*	1 to 2.5 mg/gal	Sova, 1963
Streptococcus sp.	Golden shiner *Notemigonus crysoleucas*	50 mg/gal	Robinson and Meyer, 1966

Source: Herman 1969.

Environmental Effects

Coastal or estuarine areas, not the open ocean, are the areas most likely to be affected by tetracyclines. Of the tetracyclines administered to humans, 80 to 95 percent is excreted in active form (pp. 354-357). This would, however, dilute in sewage collection and treatment systems. If 100 percent of the average therapeutic dose (1 g/day) were excreted, it would be diluted to 1.8 μg/ml by the daily per capita waste water production of 555 liters (Clark and Viessman 1969). Even if a quantity equivalent to the highest annual U.S. production of tetracyclines (2.319 tons, or 2.32×10^9 average daily human doses) were employed in human therapy, the average quantity consumed per day would be 6.4×10^6 g. Therefore, the highest annual production would permit an average of 6.4 million people or 3 percent of the population to employ tetracycline therapy at any given time. The waste water generated by the remaining 97 percent of the population would reduce the concentration in waste water to (.03)(1.8 μg/ml), or 0.054 μg/ml. This concentration is lower than the minimum concentration for *in vitro* bacteriostatic action for most species (Welch *et al.* 1954, Bullock and Collis 1969, Bohonos *et al.* 1954). Human therapeutic uses of tetracycline account for only a part of the total U.S. production.

Excreted tetracyclines are not likely to remain active in the environment. They are rapidly deactivated in aqueous solution, particularly at neutral and basic pH, and the deactivation is accelerated by elevated temperature (p. 343). In addition, tetracyclines form insoluble precipitates with multivalent cations such as Ca^{+2} and Mg^{+2}, and they bind strongly to solids containing chelating metals (e.g., $CaCO_3$ and Fe_2O_3)(Table 7-12). Therefore, they will tend to precipitate out of solution or absorb to suspended mineral particles and sediments. Any remaining in solution long enough to reach marine or estuarine waters will probably be inactive because of the relatively high concentration of Mg^{+2} and Ca^{+2}, which can reverse the antibiotic activity of tetracyclines in solution.

When these tetracyclines are used as feed additives, entire populations receive daily doses, most of which is excreted in active form. Elmund *et al.* (1971) found chlortetracycline at a concentration of 14 μg/ml in fresh manure from a feedlot where steers were fed a diet containing 70 mg/animal/day of the antibiotic. This represents an excretion rate of 75 percent. Aged manure contained 0.34 μg of chlortetracycline per gram of manure. The half-life of the antibiotic in feedlot manure was one week at 37 C and greater than 20 days at 4 and 28 C. The authors found that the antibiotic altered the microflora of the manure and caused the production of manure which was less biodegradable as measured by standard BOD procedure. They concluded that reduced stabilization rates and reduced biodegradability of manure from animals fed diets supplemented with chlortetracycline increase the potential for environmental pollution from the wastes.

TABLE 7-12

Stability Constants for the Metal Complexes of the Tetracyclines

Cation	Log K' (1:1-complex)	Log K" (2:1-complex)	Log K_3 (Overall)	Color of Complexes
Tetracycline				
Fe^{3+}	9.9	8.6	25.3[b]	Red
Al^{3+}	7.4	6.4	19.2[e]	Yellow
Cu^{2+}	7.8	5.0	12.8	Green
Ni^{2+}	6.0	5.0	11.0	Green
Fe^{2+}	5.3	4.0[a]	9.3	Red
Co^{2+}	5.4	4.4	9.8	Yellow
Zn^{2+}	4.9	ppt	(9)[f]	Yellow
Mn^{2+}	4.4	ppt	(8)[f]	Yellow
Chlortetracycline				
Fe^{3+}	9.4	7.2	22.2[c]	Red
Al^{3+}	7.2	ppt	(18)[f]	Yellow
Ni	5.8	4.7[a]	10.5	Green

(continued)

TABLE 7-12 (continued)

Oxytetracycline				
Fe^{3+}	9.6	7.2	22.5[d]	Red
Al^{3+}	7.0	ppt	(18)[f]	Yellow
Mg^{2+}	3.8	-	-	Green

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[a] Precipitation prevented direct determination. Hence log K" was obtained by subtracting log K' from log K_3 (which was found at $\bar{n}=1$).

[b,c,d,e] These values include a log K"' of 6.8, 5.6, 5.7, and 5.4 respectively.

[f] Deduced values (approximately).

Source: Albert and Rees 1956.

The major environmental hazard of the use of tetracyclines in our view involves the generation of tetracycline-resistant strains of pathogenic bacteria which may eventually reach man. Duffy (1969) suggests that the increased occurrence of drug-resistant pathogens in animals given antibiotic feed supplements may be a public health hazard. A significant proportion of strains of *Staphylococcus*, *Enterococcus*, *Klebsiella*, *Escherichia*, and *Paracolobacterium*, and most strains of *Proteus* and *Pseudomonas* are resistant to tetracyclines (Eisenberg *et al.* 1955). Wright *et al.* (1954) observed an increase in resistance to tetracyclines of *Klebsiella pneumoniae*, *Enterococcus*, *Staphylococcus aureus*, *Escherichia coli*, *Aerobacter aerogenes*, and *Streptococcus viridans* after eleven subcultures through media containing subinhibitory concentrations of tetracycline and oxytetracycline (Table 7-13). Weinstein (1970) states that, in tetracycline therapy, normal intestinal flora are suppressed and are replaced by resistant microorganisms, particularly yeasts, fecal streptococci, or *Proteus* spp. Frequently antibiotic resistant strains of *Staphylococcus* appear, and in some cases may result in fatalities (Weinstein 1970). Dukes and Dukes (1954) tested 200 pathogenic strains of *Staphylococcus aureus* isolated in 1953 from hospital patients and found 85 to 86 percent were resistant to 50 μg/ml of chlortetracycline or oxytetracycline. By contrast, the two strains of *Staphylococcus aureus* tested by Wright *et al.* (1954) were inhibited by 1.6 μg/ml of the antibiotics. These results show that resistant strains of pathogenic bacteria are being generated in tetracycline therapy; some of these tetracycline-resistant bacteria are entering sewage collection systems.

Sewage treatment effectively destroys pathogenic bacteria when the effluent is properly treated with chlorine, but sewage sludge is not disinfected and may contain large numbers of pathogenic microorganisms removed from the raw sewage by coagulation and sedimentation (Clark and Viessman 1969). The potential for return of pathogenic bacteria to humans after ocean disposal of sewage sludge is discussed in Chapter 5. In addition to sewage sludge dumping, the direct discharge of raw untreated sewage to rivers, estuaries, and the open ocean presents an opportunity for pathogens to enter food species or to be contacted through recreational activities. Brezenski *et al.* (1965) found fecal streptococcus, fecal coliform bacteria, and 12 species of *Salmonella* in

TABLE 7-13

Cross Resistance among 3 Tetracycline Analogues Resulting from 11 Subcultures in Broth Containing Tetracycline or Oxytetracycline

	Minimum Inhibiting Concentration,* Micrograms per Milliliter of:								
	Tetracycline			Oxytetracycline			Chlortetracycline		
Organism	Original	Oxy 11	Tetra 11	Original	Oxy 11	Tetra 11	Original	Oxy 11	Tetra 11
K. pneumoniae	25	400	400	25	>400	400	25	100	100
Enterococcus 1	3.1	400	50	3.1	100	50	3.1	100	25
Enterococcus 2	3.1	400	50	3.1	>400	50	3.1	100	25
Staph. aureus 1	1.6	25	12.5	1.6	6.3	6.3	1.6	25	12.5
Staph. aureus 2	1.6	3.1	12.5	1.6	3.1	12.5	1.6	3.1	12.5
E. coli	6.3	25	200	12.5	25	100	12.5	100	100
A. aerogenes	25	400	200	12.5	>400	200	12.5	100	100
Strep. viridans	1.6	3.1	25	0.8	1.6	12.5	1.6	6.3	25

* No visible growth after incubation for 18 hours at 37°C.

Original = no exposure to antibiotics; Tetra 11 = after 11 subcultures in tetracycline; Oxy 11 = after 11 subcultures in oxytetracycline.

Source: Wright *et al.* 1954.

untreated sewage, unchlorinated effluent, and in receiving waters in Raritan Bay, New Jersey. Two species of *Salmonella* were isolated from a portion of the Raritan River where the salinity was about 18 percent. Furthermore, shellfish from Raritan Bay appeared to be concentrating these bacteria (Brezenski 1965) which are one of the most important groups of human pathogens (Kabler 1959). Weinstein (1970) points out that tetracycline therapy is not uniformly effective in infections caused by *Shigella* and *Salmonella* because of the increase of strains resistant to the antibiotics. Moreover, *Escherichia coli* (fecal coliform) may be involved in certain infections (Weinstein 1970), and this species may develop resistance to tetracyclines (Eisenberg 1955).

The problem of transmission of disease by waterborne bacteria is complicated if the bacteria are resistant to antibiotic therapy. We therefore believe that it is wise to avoid using tetracyclines and other antibiotics capable of generating resistance in target organisms whenever another effective form of therapy is available.

OVERVIEW

Tetracyclines as a medicinal waste are not likely to be found in biologically active forms in the marine environment because of dilution and inactivation. Measurements of tetracyclines in the marine environment have not been reported.

There exists a possibility that tetracycline-resistant pathogenic bacteria may be shed into and disseminated in the marine environment. To the extent that such bacteria are increased by tetracycline use, they may be taken up by mollusks, and lead to increased risk of infection by humans who ingest such mollusks. Such resistant bacteria are more likely to be found in and around waters draining livestock and poultry feed lots, than in the marine environment.

On the basis of present knowledge tetracyclines do not constitute a marine pollution problem.

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TECHNETIUM - 99M

Introduction

In 1937, the Italian physicists Perrier and Segre first obtained trace amounts of technetium by bombarding molybdenum with deuterons in a cyclotron. This was the first chemical element artificially created and was offically named technetium (chemical symbol, Tc) in 1949.

All attempts to detect primordial technetium in terrestrial minerals have been unsuccessful (Alperovitch and Miller 1955, Herr 1959), because the longest-lived isotope of technetium, ^{97}Tc possesses a half-life of 2.6×10^6 years, insignificant when compared to the age of the earth. However, extremely minute quantities of technetium occur naturally in terrestrial materials, and are produced by the spontaneous fission of uranium-238, $t_{1/2} = 8.0 \times 10^{15}$ years (Kenna and Kuroda 1960). Six percent of the fission products are molybdenum-99 ($t_{1/2}$ = 67 hours) the parent of technetium-99m ($t_{1/2}$ = 6.04 hours) (Parker and Kuroda 1958).

Comprehensive reviews of the chemical and physical properties of Tc are available (Anders 1960, Koteger *et al.* 1968, Rulfs 1970).

Technetium exhibits valences ranging from +7 to -1, with the heptavalent state the most stable. In the pentavalent and tetravalent states, technetium displays a tendency to form stable complexes with organic ligands.

Two oxides of technetium are the relatively involatile TcO_2 and the volatile Tc_2O_7. Technetium dioxide can be obtained either by the reduction of aqueous solutions of pertechnetates (TcO_4^-) with zinc and hydrochloric acid, or by the pyrolysis of ammonium pertechnetate (Boyd *et al.* 1953). Although TcO_2 is unreactive in air at room temperature, it is readily oxidized by oxygen to the volatile Tc_2O_7. In additon, at 900 to 1100 C sublimation of TcO_2 occurs (Nelson *et al.* 1954).

Potassium pertechnetate ($KTcO_4$) has a solubility of 21.3 g/1000 g in water, and in the solid form, melts at 540 C and sublimes without decomposition at about 1000 C (Kotegov *et al.* 1968).

Technetium forms two sulfides, Tc_2S_7 and TcS_2, but only the heptasulfide is pertinent to this discussion. This insoluble species is obtained by passing hydrogen sulfide through acid solutions of pertechnetates. In 6N HCl, a reduction of the pertechnetate ions to lower oxidation states that are not precipitated by hydrogen sulfide begins (Boyd *et al.* 1960). In 9N HCl solutions, this reduction goes to completion.

Nuclear Properties

Technetium has no stable isotopes. Sixteen isotopes with mass numbers ranging from 92 to 107 and six isomers are presently known. The majority of Tc isotopes are formed by the irradiation of molybdenum with deuterons or protons, or molybdenum or ruthenium with neutrons. Although the isotopes of technetium have aroused much academic interest, the three shortlived isomers ^{95m}Tc (61 days), ^{97m}Tc (90.5 days), and ^{99m}Tc (6.0 hours) have the most practical value. The first two isomers are obtained by deuteron or proton bombardment of molybdenum, whereas ^{99m}Tc is formed by irradiating molybdic trioxide with neutrons in a reactor.

Technetium isotopes are also formed in large amounts from the fission of uranium, plutonium, or thorium, either directly or as a delay product of molybdenum isotopes. Of the isotopes formed, ^{99}Tc is produced in the largest amounts (6 percent) (Katcoff 1958).

Uses

The major use of technetium at the present time is in tumor localization with Tc-99m (Quinn 1964). The favorable nuclear characteristics of this nuclide are a short half-life (6 hours), a 140 Kev gamma ray, and absence of primary particle radiation.

The short half-life of Tc-99m (6 hours) lowers the irradiation dose to the organs even when the isotope is retained in the body (Harper *et al.* 1965). The pertechnetate (TcO_4^-) closely resembles iodide (I^-) in its biological fate. It is distributed rapidly in extracellular space and is specifically retained (permitting scanning) in the thyroid gland, the salivary glands, and the stomach.

Since it does not cross the blood-brain barrier appreciably, it had been used extensively in brain scanning (Anger and Gottschalk 1963).

A Tc-99m sulfur colloid is removed from the blood by the reticuloendothelial system, thus permitting visualization of the liver, spleen, and bone marrow (Harper *et al.* 1964). Harper *et al.* (1965) described other uses of technetium such as an iron complex for kidney scanning, the thiocyanate for liver scanning, and an aerosol form for inhalation studies.

Ammonium pertechnetate is a good corrosion inhibitor (Cartledge 1955). Of all elements, technetium has the highest critical temperature (temperature at which the electrical resistance of an element becomes zero). This property should make it valuable as a superconductor (Daunt and Cobble 1953), ^{99}Tc has been used to prepare standard sources of B-radiation with an energy of 0.292 MeV (Bainbridge *et al.* 1953).

The formation of Tc-99m as a decay product of the relatively longer-lived Mo-99 is important in the preparation and shipment of technetium radiopharmaceuticals to places removed from the production facility. A given quantity of ^{99}Mo is bound to an alumina column enclosed in a lead shield to form a generator. When equilibrium has been attained between the parent and daughter inside the generator, the apparent half-life of the daughter is increased to that of the parent. The required quantity of 99m-Tc may then be obtained by eluting the column with a saline solution. The molybdenum species is not affected by this procedure (New England Nuclear 1973).

Cesium-134, Rubidium-86, and Cobalt-60 have been identified as radioactive contaminants in Technetium generators and Cesium-134, Antimony-124, Zirconium-95, Niobium-95m and 95, Zinc-65, and Cobalt-60 have been identified as radioactive contaminants on the alumina column from a one-year-old Technetium generator (Podolak 1972).

Production

Molybdenum Bombardment

The U.S. production of ^{99}Mo, the parent of technetium-99m, has been estimated by General Electric Corporation (GETR) of California to be 500 Curies (C2)/week of high specific activity, and 720 Ci/week of low specific activity (so-called instant technetium). The high specific activity ^{99}Mo is sent to radiopharmaceutical houses for the construction of technetium generators. The low specific activity ^{99}Mo is shipped in dosage amounts to hospitals and doctors. The total ^{99}Mo production, when converted into the amount of Tc-99 (t-1/2 = 2.1 x 10 yrs) produced by commercial companies, is approximately 2.3m Ci/yr or 135 mg Tc/yr since the specific activity of technetium is 17 m Ci/g. Figure 7-6 shows the expected increase in use of Tc-99 as a radiopharmaceutical in the United States.

Weapons Testing

The world fallout of technetium-99 has been estimated by the Health and Safety Laboratory (HASL), U.S. Atomic Energy Commission as 4,800 Ci through 1972 (Harley 1973, pers. comm.)

Using a global surface area of 5.1 x 10^8 km^2 and assuming the uniform deposition of the isotope, we estimated a world fallout of 9.4 x 10^{-3} mCi/km^2. This value implies that the U.S., which occupies 2 percent of the total world surface area, has received 96 Ci of Tc-99 fallout.

Nuclear Reactors

The Tc-99 content of the spent fuel of both a Liquid Metal Fast Breeder Reactor (LMFBR) and a Liquid Water Reactor (LWR) have been calculated (Table 7-14).

Technetium-99 is available in research quantities from Oak Ridge National Laboratories, Oak Ridge, Tennessee, where the isotope is recovered directly from fission product waste solutions.

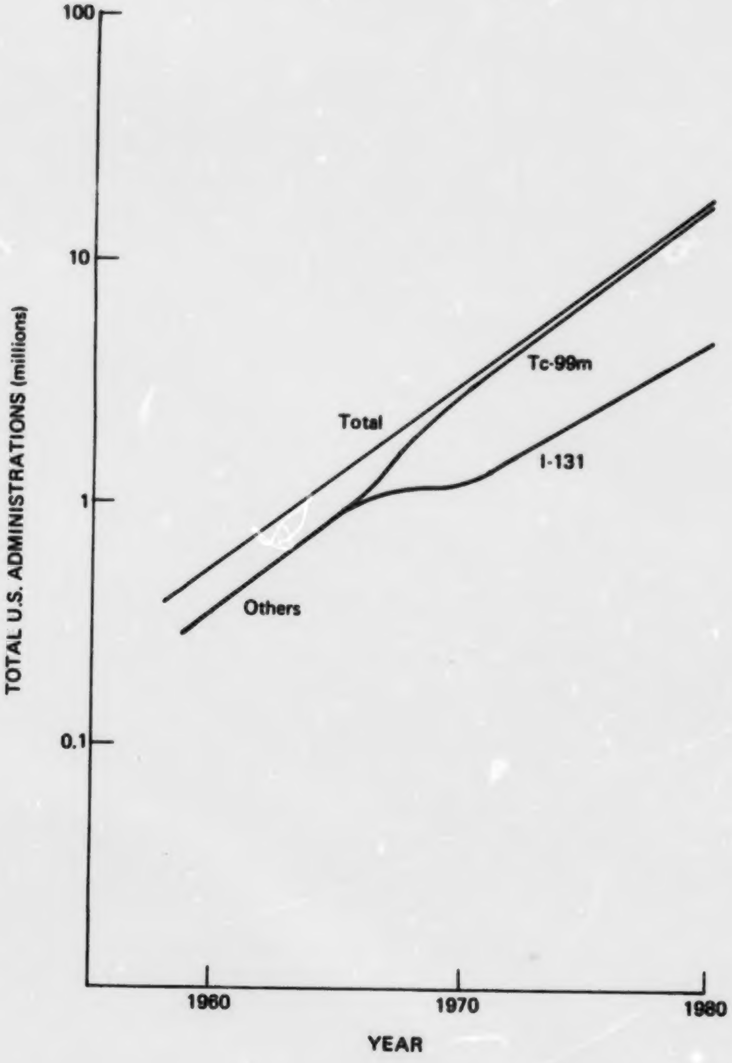


FIGURE 7-6

Projected Use of Radiopharmaceuticals in the United States

TABLE 7-14

Spent Reactor Fuel TC-99 Content

Reactor Type	Power (Mw/Mt)	Tc-99 Produced (Ci/Mt)
Liquid Metal Fast Breeder Reactor	58.23	4.05
Light Water Reactor	30.00	3.83
High Temperature Gas Reactor*	30.00	3.83

*High Temperature Gas Reactor assumed identical characteristics to Light Water Reactor

(Projected) Thousands of Curies Tc-99 Present in Reactor Fuel

	Total		Light Water Reactor High Temperature Gas Reactor		Liquid Metal Fast Breeder Reactor	
Year	U.S.	Foreign	U.S.	Foreign	U.S.	Foreign
1980	17	18.2	17	18.2		
1985	36.2	39.0	36.1	38.7	0.1	0.3
1990	64.0	73.5	62.4	71.3	1.6	2.2
2000	132.0	165.0	104	136	28	29

Source: USAEC 1972.

Initially, 1.2 kg of Tc were to be produced per year by the Oak Ridge National Laboratory Fission Product Recovery Plant (Boyd 1959), but research demand for it has never fully materialized and orders are filled from past production stockpiles.

Releases

We classified U.S. releases of technetium to the environment as either USAEC-controlled or non-USAEC controlled. Activities of concern in the former category are explosions of nuclear devices, leakages of nuclear reactors, and releases of isotopes from nuclear fuel reprocessing plants. Among the radiation sources specifically not regulated by the USAEC are: accelerator-produced radioisotopes, excreta from patients administered radiopharmaceuticals, and hospital generators.

Many states have accepted regulatory responsibility from the USAEC governing the use of radioisotopes and have instituted policies governing radiation aspects not covered by USAEC regulations (Table 7-15).

USAEC Controlled

Nuclear Devices The amounts of technetium released to the world's atmosphere are discussed under Production (p. 383). We expect, because of the observance of the Partial Test Ban Treaty (1964), that the cited value of 4800 Ci TC for the world's surface area will not be substantially increased. Transport of the isotope to the earth's surface occurs through precipitation. Attrep *et al.* (1971) found that the concentration of Tc-99 varied between 0.14×10^{-2} and 1.7×10^{-2} pCi/liter for 13 rain samples collected in 1967.

Reactors and Reprocessing Facilities Figure 7-7 predicts the yearly production of Tc-99 from 1960 to 2000. The data points between 1960 and 1980 were calculated by the equation of Kotegov *et al.* (1968), which relates the power of a reactor to the mass of technetium produced.

Loss to Soil The U.S. Atomic Energy Commission's Separations Plants at Hanford, Washington, have discharged large volumes of intermediate and low-level radioactive liquid wastes into the ground for approximately 30 years. It has been estimated that 4,000,000 curies of beta-emitting isotopes have been sent to soil retention through 1971. Of this quantity 200,000 remain, allowing for decay (Warren 1972). Between January 1952 and January 1956, 1.5×10^8 liters of waste liquid were discharged to the

TABLE 7-15

Agreement States/Scope of Isotope Regulations

	Regulations on Radium	Isotope Generators	Accelerator Produced Isotopes	Nuclear Medicine Patent Excretions
New Hampshire	x	x	x	
New York	x	x	x	
Maryland	x	x	x	
Alabama	x	x	x	
Florida	x	x	x	
Georgia	x	x	x	
Kentucky	x	x	x	
Mississippi	x	x	x	
North Carolina	x	x	x	
South Carolina	x	x	x	
Tennessee	x	x	x	
Arkansas	x			
Louisiana	x			
Texas	x	x		
Kansas	x	x	x	
Nebraska	x	x	x	
Colorado	x	x	x	x
North Dakota	x	x	x	
Arizona	x	x	x	
California	x	x	x	
Nevada		x	x	
Idaho	x	x	x	
Oregon	x	x	x	
Washington	x	x	x	

Source: Miller 1973.

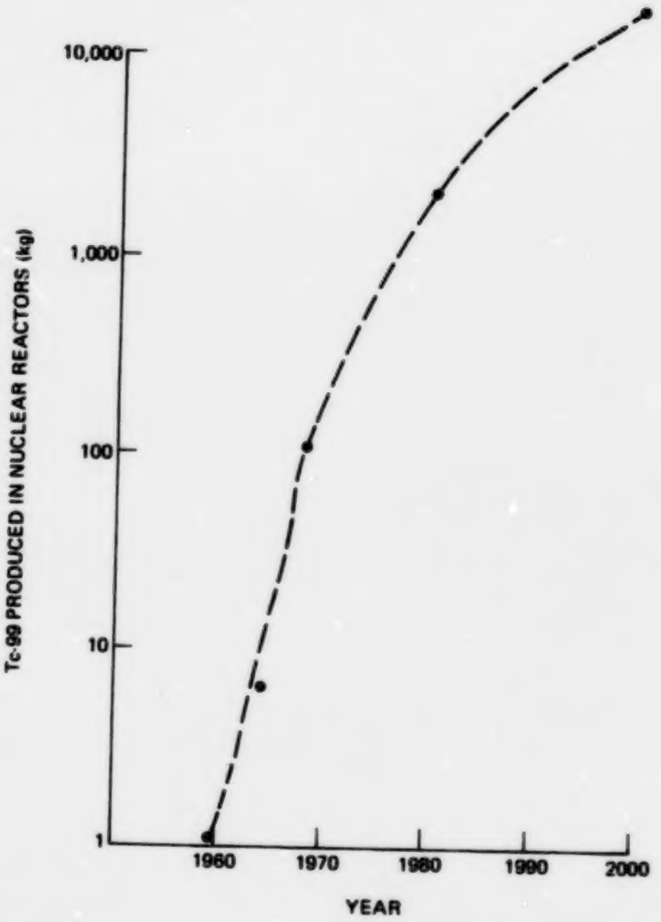


FIGURE 7-7

Amount of Tc-99 Produced in Nuclear Reactors, U.S. and Europe ground from the 216-Si and 2 crib sites (Brown 1967). Contained in these wastes were an estimated 750,000 beta curies of mixed fission products. The migration of the radionuclides through the underlying sediments was detected by a network of wells and monitoring equipment. Although the quantity of Tc-99 discharged in this manner was not given, Figure 7-8 was presented to show the groundwater seepage pattern for this isotope in addition to ^{106}Ru and ^{3}H. Brown (1967) concluded from this study that tritium, ruthenium-106, and technetium-99 are not readily sorbed on sediments and, hence, migrate at the same speed as groundwater.

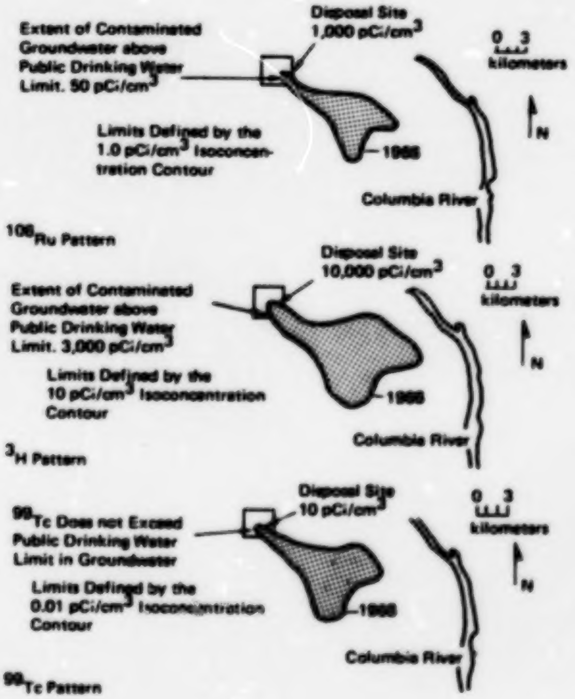
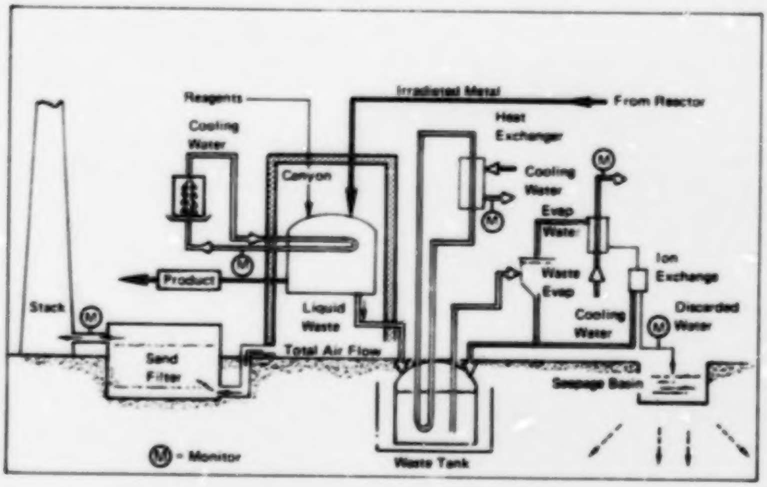

Disposal Site 1,000 pCi/cm^3
Extent of Contaminated Groundwater above Public Drinking Water Limit. 50 pCi/cm^3
0 3 kilometers
N
Limits Defined by the 1.0 pCi/cm^3 Isoconcentration Contour
1966
Columbia River
^{106}Ru Pattern
Disposal Site 10,000 pCi/cm^3
Extent of Contaminated Groundwater above Public Drinking Water Limit. 3,000 pCi/cm^3
0 3 kilometers
N
Limits Defined by the 10 pCi/cm^3 Isoconcentration Contour
1966
Columbia River
^{3}H Pattern
Disposal Site 10 pCi/cm^3
^{99}Tc Does not Exceed Public Drinking Water Limit in Groundwater
0 3 kilometers
N
Limits Defined by the 0.01 pCi/cm^3 Isoconcentration Contour
1966
Columbia River
^{99}Tc Pattern

FIGURE 7-8

Groundwater Contamination Patterns Resulting from Disposal of Radioactive Liquid Wastes at a Hanford Production Site

Unruh (1972) has presented more recent data on the migration of the tritium (t-1/2 = 12 years) waste plume toward the Columbia River. Although Tc was not mentioned in the study, Figure 7-8 indicates that thr tritium plume would be a good approximation of the migration of technetium. From these data, it appears that Tc will reach the nearby river.


Reagents
Irradiated Metal
From Reactor
Cooling Water
Heat Exchanger
Canyon
Cooling Water
Evap Water
Product
Waste Evap
Ion Exchange
Stack
Liquid Waste
Cooling Water
Discarded Water
Total Air Flow
Sand Filter
Seepage Basin
Ⓜ = Monitor
Waste Tank

Source: USAEC, Savannah River Plant 1973.

FIGURE 7-9

Savannah River, South Carolina Water Separation Process

Although Tc-99 is not routinely monitored by the USAEC at the Savannah River, South Carolina Plant, an estimate of its release can be made. The liquid from the waste tank enters an evaporator for primary separation (Figure 7-9). The vapor from this process is condensed and passed through an ion-exchange resin before going to the seepage basin. As previously stated, Tc-99 is a high-yield fission product (6 percent), and would be expected to be present in the liquid wastes in relatively large quantities. After a cooling period, the alkaline wastes separate into a thin layer of sludge in the bottom of the waste tank and a body of clear liquid above it. Although Cesium is known to remain in solution, technetium should also be present since the solubility of $KTcO_4$ is 21.3 g/liter. Such a high solubility would also indicate transport of the isotope with Cs from the bulk solution in the evaporator to the water vapor and to the condenser. Although Cs would be expected to be sorbed by the zeolite ion-exchange resin, this would not be the case for the negatively charged pertechnetate ion (TcO_4^-). The isotope could then enter the seepage basin and migrate through the sediments. Such an occurrence might be expected for any facility employing this method of disposal.

Loss to Rivers and Oceans Although the direct-cooled plutonium production reactors at Hanford, Washington, discharged 10,000 Ci of ^{99}Tc (6.0×10^2 kg) into the Columbia River system before their shutdown in 1970 (Foster 1973), the escape of this material from present day U.S. reactor facilities has been estimated to be insignificant (USAEC-ORNL April, 1972). However, likely sources of technetium discharges into the world's aquatic environments are other nuclear fuel reprocessing plants, such as Windscale in England, which employ ocean outfalls for waste disposal (Table 7-16).

Although technetium is not mentioned in the waste data, a case can be made for its release. Table 7-17 lists the average composition of waste solutions resulting from the Purex and Redox processes (Boyd 1959). The ratio of ^{106}Ru to ^{90}Sr in the wastes of the Purex process is approximately 2:1, and from the Windscale wastes, the ratio is 2.9:1. The similarity of the two ratios implies that separation techniques may not be complete before discharge. If this is true, the highly soluble, poorly sorbed technetium species would also be discharged. Assuming that 41 mg of Tc are discharged for every 4.6 Ci of ^{90}SR (Table 7-17), and since 1.23×10^4 Ci of ^{90}SR were discharged from Windscale in 1971, 0.11 kg of Tc were probably released from this plant in that time period. Information concerning other foreign reprocessing facilities is not available.

TABLE 7-16

Radioactive Waste Discharge at Windscale, England

Radioactivity	Authorized Discharge (Ci/yr)	Amount Discharged (Ci/yr)
Total Beta	300,000	160,000
Ru-106	60,000	36,000
Sr-90	30,000	12,000
Total Alpha	6,000	2,700

Source: Preston 1973.

Technetium-99 is also released to the environment through laboratory drains. Golchert and Sedlet (1969) collected surface water samples below the Argonne National Laboratory outfall (Sawmill Creek) and found an average of 4.65 p Ci/liter 99Tc in 20 percent of their 150 samples.

Loss to the Atmosphere Figure 7-10 illustrates the molten-salt fluoride volatility process employed in the reprocessing of spent uranium fuel (Oak Ridge National Laboratroy 1971). After dissolution of the fuel element, purified fluorine flows into the fluorinator (FV-100). Volatile fission product fluorides, VF$_6$, and unreacted fluorine pass out of the fluorinator through the movable bed absorber (FV-105); the fluorides of most of the fission products are non-volatile and remain in the salt. The gas stream passes through a section of the movable bed absorber containing NaF pellets at 400 C. Here, the bulk of the fission product fluorides that were volatilized or entrained are deposited; the F$_2$ and essentially all of the U, Mo, Np, and Tc, and significant quantities of Zr, Nb, Ru, I$_2$ and Te proceeded to the next section containing NaF pellets at 150 C. The UF$_6$ and most of the contaminants are sorbed under these conditions, while the fluorine, MoF$_6$ and some tellurium fluorides pass on to the chemical trap (FV-121), which contain NaF at ambient temperature. The MoF_6 and any traces of VF_6 are removed by this trap. TcF_6 was not mentioned as being removed by this trap, and Table 7-18 indicates that technetium may escape this isolation step, and proceed to the caustic scrubber and, finally, to the stack. TcF_6 is soluble in alkaline solutions, hydrolyzing to form a black precipitate of technetium dioxide and pertechnetates; however, no kinetic data are available on this process and release to the atmosphere may be possible.

TABLE 7-17

Composition of Waste Solutions Containing Technetium

Component	Redox Process	Purex Process
$Al(NO_3)_3$	1.4M	--
NH_4NO_3	1.9M	--
$Hg(NO_3)_2$	0.0125M	--
HNO_3	--	3.9M
^{137}Cs	8.87 Ci/l	4.4 Ci/l
^{90}Sr	0.94 Ci/l	4.6 Ci/l
^{100}Ru	0.10 Ci/l	9.0 Ci/l
^{144}Ce	0.87 Ci/l	88.7 Ci/l
^{147}Pm	1.06 Ci/l	17.0 Ci/l
^{99}Tc	6.5 mg/l	41 mg/l

Source: Boyd 1959

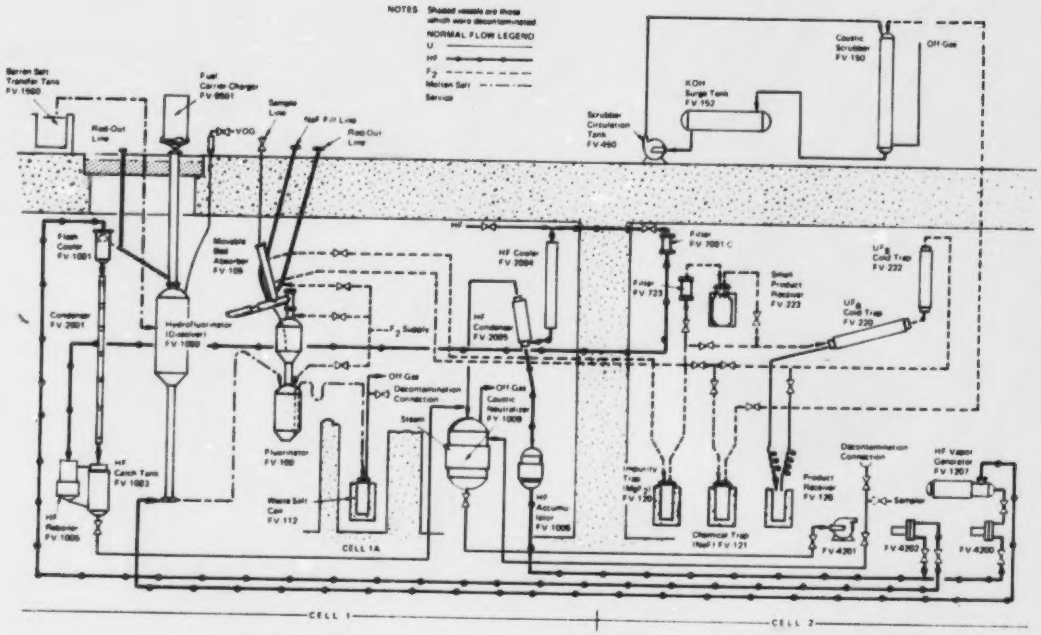

NOTES Shaded vessels are those which were decontaminated
NORMAL FLOW LEGEND
U
HF
F2
Molten Salt
Service
Barren Salt Transfer Tank FV 1960
Fuel Carrier Charger FV 8501
Rod-Out Line
VOG
Sample Line
NaF Fill Line
Rod-Out Line
Scrubber Circulation Tank FV 490
KOH Surge Tank FV 152
Caustic Scrubber FV 190
Off Gas
Flash Cooler FV 1001
Movable Bed Absorber FV 105
HF
HF Cooler FV 2004
Filter FV 7001 C
Filter FV 723
Small Product Receiver FV 223
UF6 Cold Trap FV 222
UF6 Cold Trap FV 220
Condenser FV 2001
Hydrofluorinator (Dissolver) FV 1000
F2 Supply
HF Condenser FV 2005
Off Gas
Decontamination Connection
Off Gas
Caustic Neutralizer FV 1009
Steam
Fluorinator FV 100
HF Catch Tank FV 1003
HF Reboiler FV 1005
Waste Salt Can FV 112
CELL 1A
HF Accumulator FV 1006
Impurity Trap (MgF2) FV 120
Chemical Trap (NaF) FV 121
Product Receiver FV 130
Decontamination Connection
Sampler
HF Vapor Generator FV 1207
FV 4201
FV 4202
FV 4200
CELL 1
CELL 2

FIGURE 7-10

Source: U.S. Atomic Energy Commission 1971.

Schematic Flowsheet of Equipment in Volatility Pilot Plant

TABLE 7-18

Vapor Pressure of TcF_6

Pressure (mmHg)	59	78	100	115	140	760
Temperature (C)	0	4.9	9.3	1.20	15.7	55.3

Source: Kotegov *et al.* 1968.

Figure 7-11 shows the estimated amount of technetium which could be discharged annually to the environment for various assumed releases.

Non-USAEC Controlled

Although information concerning the release of ^{99}Tc from hospitals is almost nonexistent, Moss (1972) has indicated that both ^{131}I and ^{99m}Tc are found in hospital and sanitary sewage system effluents (Table 7-19). He further states that these two isotopes represent approximately 2 percent of the isotopes ordered by the hospitals in Allegheny County, Pennsylvania. If we assume that this value holds for all hospitals in the U.S., and if the material not used is disposed of in an approved manner, the minimum percent of technetium-99 released to the environment via patient excreta is 92 percent or 124 mg/year (calculated from the General Electric production estimates). We assume that this value would increase at the same rate as Tc usage in the coming years (Figure 7-6).

Technetium-99 and manganese-5[illegible] exist as colloidal forms with particle-size 0.1 microns in seawater (Tikhomirov *et al.* 1970). It appears likely that Tc and Mn are coagulated or converted by biochemical processes in microorganisms into complex organic compounds which are easily sorbed on suspended matter.

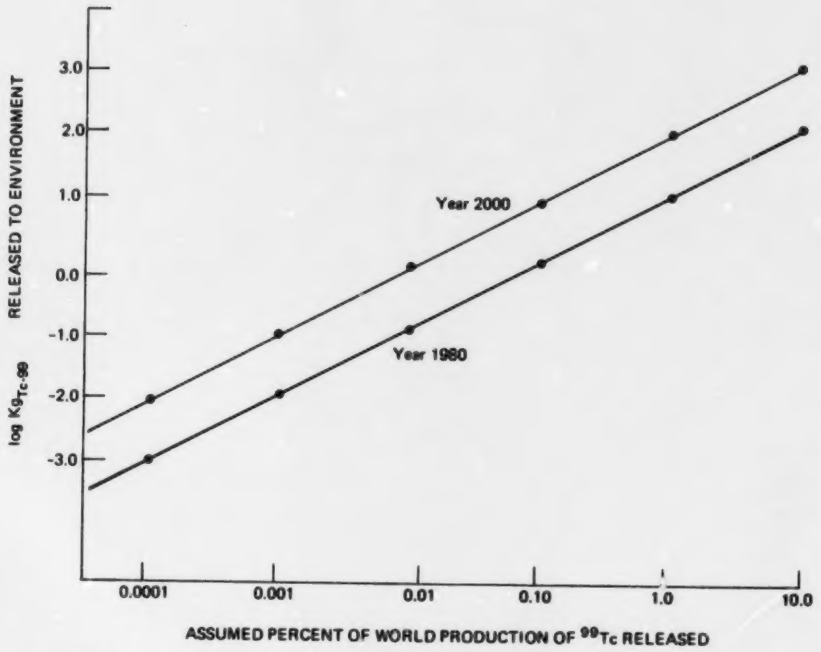


FIGURE 7-11

Calculated Release of ^{99}Tc for Projected Production Levels

TABLE 7-19

Comparison of Input and Usage of ^{99m}Tc for one Hospital

Year	Ordered (mCi)	Used (mCi)	Percent Released
1969	2,255	2,205	98
1970	3,711	3,540	95
1971	4,800	4,418	92

Source: Moss 1972.

Higher uptake of technetium by zooplankton than phytoplankton has been reported (Tikhomirov *et al.* 1970). This was interpreted to indicate that the element is assimilated both directly from seawater and from digested phytoplankton. The uptake of the isotope was increased by the presence of iron. It was postulated that the iron hydrolysis products, which are known to concentrate microelements of their surface, facilitate the assimilation (Tikhomirov *et al.* 1970).

Gearing and van Baalen (1973) have performed preliminary studies of the effect of technetium on various algae (Tables 7-20 and 7-21). The authors suggest that the interaction of technetium with blue-green algae results in destruction of the pigment C-phycocyanin. The above study was primarily concerned with algae growth on a short-time scale only.

OVERVIEW

Technetium-99m is an example of a group of artificially produced radioisotopes, the uses of which are expanding. The ways this isotope is being used in medicine and industry today do not seem to pose any threats to the marine environment. Nonetheless, the lack of knowledge about the leakages from hospitals and industrial sites suggests that occasional monitoring of the amounts of the daughter, ^{99}Tc in the coastal marine environment in areas close to major population and use centers is warranted.

TABLE 7-20

Technetium Toxicity to Algae

Algae	Lethal Technetium Concentration (ppm)
Agmenellum quadruplicatum	300
Macrozamia (In Light)	160
(In Dark)	120
Phormidum	80
3H Thallasiosira	270
Duniella	620

Source: Gearing and van Baalen 1973.

TABLE 7-21

Coccochloris clabens Growth Rate and Lag-Time Variation with Pertechnetate Concentration. Cell Density when NH_4TcO_4 added: 1.2×10^5 cells/ml.

(TcO_4^-); ppm	K*	Lag Relative to Control, hours
0.00	1.65	--
16.2	1.55	1.0
18.4	1.65	3.0
20.5	1.60	4.5
22.6	1.50	7.0
24.7	1.60	15.0
32.4	1.50	49.0

$$*K = \frac{\log_{10}(N_t/No)}{t}$$

There K = growth rate

t = time
No = number of cells at time zero
Nt = number of cells at time t

Source: Gearing and van Baalen 1973.

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CHAPTER 8

MARINE LITTER

Workshop Panel

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Background Paper

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INTRODUCTION

We define marine litter as solid materials of human origin which are discarded at sea or reach the sea through waterways, or through domestic and industrial outfalls. It may include plastics, paper, glass, metals, lumber, or trees, and may vary in size from meters to microns in length or diameter. Litter is concentrated at physical boundaries in the ocean, and may float and ultimately be deposited on shore, break up, become suspended in the ocean, decompose, settle to the ocean floor, or be ingested by marine organisms. Its persistence in the ocean is highly dependent on the nature of the object, where it was discarded, and on the oceanic conditions to which it is subject.

Rapidly degradable materials such as vegetable and food wastes, materials which are placed to make artificial reefs, and wrecks were not considered. Materials which are deliberately disposed of at sea as a part of a regulated ocean dumping program are considered in Chapter 5. Petroleum residues such as tar balls were excluded, because these substances are considered in separate reports.

At this time, the most direct effect of marine litter is its appearance on beaches and shorelines. Aside from its aesthetic damage, litter may physically injure organisms and humans, and physically damage ships and machinery. Occasionally plastic sheets are picked up in water intakes of ships, and ropes and nets may foul propellers resulting in mechanical damage or delay.

Extensive effects of litter on marine life have not been reported, although a number of mechanisms by which litter can cause biological damage have been demonstrated.

We estimated the litter input to the ocean by multiplying the number of people at sea engaged in a given activity by the average amount of trash that the activity generates. Separate estimates were made for sources such as bulk cargo handling. The likely routes of removal of litter from the oceans were estimated based on the known physical properties of the materials.

We considered two classifications of litter that are generated by human activities: domestic and commercial refuse. Domestic refuse consists mostly of packaging materials, including paper, plastics, glass, and metals. We estimated the onshore generation rate of domestic litter to be 1.6 kg/person/day (Table 8-1), and the shipboard litter generation rate to be 0.8 kg/person/day (Table 8-2). Tables 8-1 and 8-2 also show the percentage composition of the categories of litter. The amount of commercial refuse, such as cargo associated wastes and lost fishing gear reaching the oceans, was estimated based on studies of the various activities.

SOURCES

Rivers and Bays

Cut lumber, deteriorating docks and pilings, and trees are a type of marine litter which may be a navigational hazard. Information concerning the amount of navigational debris which has been removed from certain

U.S. ports has been collected by the Corps of Engineers and the Coast Guard as shown in Table 8-3. Preliminary results of a study on large floating debris in harbors and inshore areas (currently being conducted for the Coast Guard by the Battelle Institute) indicate that these objects are to a great extent milled or nonmilled wood, and that the dominant form varies with region (Jacobs 1973, pers. comm.).

TABLE 8-1

Onshore Refuse Generation Factors

	Generation Factor
Total refuse generation[1]	2.2 kg/person/day
Total amount in litter category[2] (71.1 percent)	1.6 kg/person/day

Material	Percent
Paper	72.0
Glass	12.0
Metal	11.7
Cloth	1.8
Plastics	1.8
Rubber	0.7
	100.0

Sources: 1. Smith and Brown 1971.

2. Pratt *et al.* 1973 (total refuse less food and vegetable wastes).

TABLE 8-2

Shipboard Refuse Generation Factors[1]

	Generation Factor
Total Refuse Generation	
IMCO, U.S., 1972	1.9 kg/person/day
IMCO, U.S.S.R., 1972	1.1
IMCO, Japan, 1972	2.6
U.S. Department of Defense 1971	1.4
AVERAGE	1.75 kg/person/day
Total amount in litter category[1] (46 percent)	0.8 kg/person/day

Material	Percent
Paper	63.0
Metal	16.6
Cloth	9.6
Glass	9.6
Plastics	0.7
Rubber	0.5
	100.0

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[1] Total refuse less food and vegetable wastes.

Passenger Vessels

We estimated the number of person-days at sea attributable to passenger liners by obtaining schedules for principal passenger ships which gave numbers of passengers and the length of time spent between ports, and by adding crew complements. Crew sizes were obtained directly from the ship companies for a number of ships, and an estimate of half the maximum passenger capacity was used for others (Table 8-4). We used the estimate for trash-generation onshore (1.6 kg litter/person/day) for people aboard

TABLE 8-3

Amounts of Navigational Debris Removed from Harbors

Area	Year	Amount 10^6 kg/yr	Source
New York Harbor	1969	14.0	Scharf 1973, pers. comm.
	1970	14.5	
	1971	16.9	
	1972	16.9	
Baltimore	1970-1972	1.2 to 1.5	O'Hagan 1973, pers. comm.
Potomac/ Anacostia	1966-1972	2.3 to 3.2	Howard 1973, pers. comm.
Norfolk		1.4	Lawless 1973, pers. comm.
San Francisco	1969	8.0	Thomas 1973, pers. comm.
	1970	6.6	
	1971	6.5	
	1972	7.8	
Delaware Bay	1972-1973	2.5	Caccese 1973, pers. comm.
Seattle, Washington	1968	1.7	Latta 1973, pers. comm.
	1969	4.0	
	1970	3.2	
	1971	2.0	
	1972	2.9	
	1973	2.6	
Seattle, Washington	1971	10.1	Log Patrol: Cole 1973, pers. comm.
	1972	7.9	
	1973	7.1	
New Orleans	(none)[1]		Campbell 1973, pers. comm.

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[1] New Orleans collects only sunken hazards.

TABLE 8-4

Gross Tonnage Per Passenger and Per Crew for Selected Passenger Vessels

Vessel	Gross Tons	Passengers	Crew[1]	Gross Tons Per Passenger	Gross Tons Per Crew Member	Passenger to Crew Ratio
Cunard Adventurer	14,000	700	425	20	33	1.6
Cunard Ambassador	14,000	700	425	20	33	1.6
Gripsholm	22,726	450	250	51	91	1.8
Homeric	25,387	625	400	41	63	1.6
Island Princess	20,000	600	--	33	--	--
Kungsholm	26,678	500	250	53	107	2.0
Nieuw Amsterdam	38,987	1,100	600	35	65	1.8
Olympia	17,420	750	350	23	50	2.1
Princess Italia	12,000	400	--	30	--	--
Queen Anna Maria	21,715	750	350	29	62	2.1
Queen Elizabeth 2	65,863	2,000	1,000	33	66	2.0
Rotterdam	37,783	1,106	600	34	63	1.8
Sea Venture	20,000	650	300	31	67	2.2
Statendam	25,000	732	440	34	57	1.7
Veedam	23,000	610	356	38	65	1.7
Volendam	23,000	610	356	38	65	1.7
AVERAGE	25,472	768	436	34	63	1.8

[1] Obtained by phone from ship companies 1973.

passenger liners. Using this value and 1.7 x 10^7 person-days/year, we computed an estimate of 2.8 x 10^4 tons per year of litter associated with passenger vessels (Table 8-5). This is probably an under-estimate because data were limited to ocean ships serving U.S. ports and did not include coastal vessels.

TABLE 8-5

Estimated Trash Generated by Major Passenger Liners Serving United States Ports

Area		Man-Days/Year (x 10^6)	Estimated Amount of Trash/Year[1] (10^6 kg)
Caribbean		6.0	9.6
Mediterranean		1.5	2.4
North Atlantic		7.5	12.0
South Atlantic		0.5	0.8
Pacific		1.8	2.9
	TOTAL	17.3	27.7

[1] Assumes 1.6 kg trash generated per man-day.

Merchant Shipping

Merchant shipping activity involves cargo freighters, tankers, and intercoastal barges. Litter sources are vessel crews and cargo-associated debris.

To estimate the number of ships at sea, we used the U.S. Department of Defense (1964) sightings which give ship density in 5° longitude and 5° latitude areas (Table 8-6). The total number of ships at sea at a given time, 9,101, is an over-estimate because it includes other than merchant vessels. Eighty percent of the vessels sighted were within 400 km of land. We used an estimate of 40 for crew size (Intergovernmental Maritime Consultative Organization, hereinafter referred to as IMCO, U.S. 1972; IMCO, Canada 1972). The total estimated crew is thus 3.8 x 10^5 on any given day or 1.4 x 10^8 person-days per year.

TABLE 8-6

Average Ship Sightings, 1964

Oceanic Region	Number of Ships Sighted per Day[1]	Estimated Number of Crew/Day[2]	Estimated Amount[3] of Trash (10^6 kg/yr.)
Indian Ocean	1,189	47,560	13.9
Indonesia	761	30,440	8.9
South Pacific	461	18,440	5.4
North Pacific	1,196	47,840	14.0
North Atlantic	2,890	115,600	33.8
South Atlantic	567	22,680	6.6
Mediterranean	1,035	41,400	12.1
North Sea	515	20,600	6.0
Gulf of Mexico	133	5,320	1.6
Caribbean	354	14,160	4.1
TOTAL	9,101	364,040	106.4

[1] U.S. Department of Defense 1964, sightings which give ship density in 5° longitude and 5° latitude areas.

[2] (Number of ships sighted per day) (average crew of 40/ship).

[3] 0.8 kg/crew/day.

Using 1.4 x 10^8 person-days/year and a shipboard litter generation rate of 0.8 kg/person-day, we estimated 1.1 x 10^5 tons*/year for merchant vessel crew-associated litter.

Cargo-associated wastes from merchant shipping include dunnage, shoring, pallets, wires and plastic covers. Cargo wastes have been estimated at 285 tons/ship/year (IMCO, U.S. 1972).

Of the 4.7 x 10^4 merchant vessels registered, 1.96 x 10^4 are ocean-going and greater than 10^3 gross tons (Anonymous [Marine Engineering Log] 1971). If each of these is assumed to generate 285 tons of cargo-associated waste, an estimated 5.6 x 10^6 tons/year result. An unknown fraction of these wastes is released in or near ports.

Recreational Boating

Recreational boats include pleasurecraft, sports, and certain fishing vessels. The number of recreational boats registered in the United States was estimated by the U.S. Department of Transportation (1972) to be 6 x 10^6. Approximately 50 percent of the total registered boats were from states bordering marine waters. There was no data breakdown to indicate whether the boats were used in marine or in freshwaters. We assumed that 33 percent were used in marine waters (1 x 10^6 vessels).

We based our estimate of world recreational boating on Gross National Product (World = U.S. times 3) and thus used a value of 3 x 10^6 recreational boats using marine waters for the world. No data are available to assess the accuracy of this estimate or regional distribution of these vessels.

The average recreational boat made 2.5 trips of 5.66 hours per week with 3.59 passengers for 22 weeks per year in the Northern U.S. and 52 weeks per year in the Southern U.S. (U.S. Congress 1967). Using these estimates we derived values of 45 person-days/year/boat in the Northern

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*All units are metric unless otherwise specified.

U.S. and 107 person-days/year/boat in the Southern U.S. We used the average of these values (76 person-days/year/boat) and a trash-generation rate of 0.453 kg/person-day (U.S. Congress 1967).

We estimated the amount of marine litter attributable to recreational boating to be 1.03 x 10^5 tons/year using the values derived above ([3 x 10^6 boats][76 person-days/year/boats][0.453 kg/person-day]).

Commercial Fishing

According to the Food and Agriculture Organization of the United Nations, hereinafter referred to as FAO (1971), approximately 1.2 x 10^5 registered vessels, over 5 gross tons, are engaged in fishing for various countries (Table 8-7). We assumed an average crew complement of 20 per vessel (U.S. Department of Commerce 1972a, Ristori 1973), and the length of the fishing season to be two-thirds of the year (240 days). Using 5.8 x 10^8 person-days/year ([1.2 x 10^5 vessels][20 persons/vessel][240 days]) and a shipboard generation rate of 0.8 kg/person-day (Table 8-2), yields a total of 4.6 x 10^5 tons/year of litter.

We also estimated fishing activity by taking the regional estimates of the world fishery catch (Herring and Clarke 1971) and dividing this by the catch tonnage per crew-day from U.S. data (0.19 tons fish caught/crew-day) (Table 8-8) and using the shipboard generation rate of 0.8 kg/person-day. This yielded 2.8 x 10^8 person-days/year or 2.2 x 10^5 tons of litter/year (Table 8-9). We used the average (3.4 x 10^5 tons/year) of these two figures for our estimate.

Another source of debris from commercial fishing is the loss of fishing equipment such as polypropylene and nylon long lines, gill nets, and floats (Andersen 1973). If 1.07 x 10^3 ships in the Alaskan Gulf in 1972 lose 1.2 x 10^4 kg/year (U.S. Department of Commerce 1972a and 1973b), then 1.2 x 10^5 ships (Table 8-7) in the world fleet could lose 1.35 x 10^3 tons/year.

TABLE 8-7

Number of Vessels in Fishing Fleets[1]

Region	Country	Number of Vessels
Asia	Mainland China	n.i.
	Taiwan	6,190
	Japan	25,974
	Philippines	1,453
Europe	Belgium	338
	Denmark	4,000
	Finland	5,608
	France	1,825
	Spain	3,968
	Germany	118
North Atlantic	Iceland	765
	Norway	5,747
	Netherlands	998
	England, Scotland, Ireland	2,442
	Canada	10,966
	U.S.	12,830
Pacific	Canada	3,549
South America	Argentina	345
	Chile	366
	Peru	2,229
	Ecuador	418
	Mexico	1,595
Mediterranean	Greece	767
	Italy	3,067
	TOTAL	95,558
U.S.S.R.		n.i.
	(estimate for U.S.S.R. and China)	25,000
		120,558 vessels

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[1] Only vessels which were steam or motor powered, and greater than 5 gross tons, were counted.

Source: Derived from data published by FAO 1971.

TABLE 8-8

U.S. Fish Catch Per Unit Effort

Area	Number of Fishermen	Catch (10^6 Tons)	Tons per Crew-Day[1]
North Atlantic	3,537	2.84	.33
Mid-Atlantic	2,129	0.69	.13
Chesapeake	4,066	1.77	.18
South Atlantic	3,339	1.59	.20
Gulf of Mexico	13,163	8.07	.25
Pacific	17,759	5.98	.14
Hawaii	315	.05	.07
		AVERAGE	0.19 tons/crew-day

[1] Assumes 240 work days per year.

Source: Derived from data published by U.S. Department of Commerce 1972b.

Military Activity

We estimated the litter generated by military activity by compiling the crew complement of the navies of the world from "Janes' Fighting Ships" (Blackman 1973) (Table 8-10). Estimates of world naval distributions were obtained from Finkelstein (1973, pers. comm.) and Fairhall (1971). Approximately one-third of the U.S. fleet is at sea at any given time (Finkelstein 1973, pers. comm.), and we assumed this ratio for all other countries. We estimated the total person-days of military activity to be 9.25 x 10^7 (Table 8-10). Using the shipboard generation factor of litter (0.8 kg/person-day) and 9.2 x 10^7 person-days/year yields a value of 7.36 x 10^4 tons/year for military activities.

TABLE 8-9

Estimate of Fishing Activity from the World Fish Catch

Region	Annual Catch[1] (10^6 tons)	Equivalent crew-days/year[2] (10^6)	Estimated Amount[3] produced per year (10^6 kg)
Indian Ocean	2.1	11	9
Indonesia	2.0	11	9
South Pacific	11.6	61	49
North Pacific	15.6	82	66
North Atlantic	5.6	29	23
South Atlantic	3.8	20	16
Mediterranean	1.1	6	5
North Sea	10.2	54	43
Gulf of Mexico	0.7	4	3
Caribbean	0.6	3	2
TOTAL	53.3	281	225

[1] Herring and Clarke 1971.

[2] Assumes 0.19 tons/crew-day (Table 8-8).

[3] Using shipboard generation factor of 0.8 kg/person/day.

TABLE 8-10

Distribution of Military Personnel on the World's Seas[1]

Area	Total Ship Complements	Person Days at Sea/Year[2] $(x10^6)$
Indian Ocean	22,400	2.7
Mediterranean & Red Sea	107,100	12.8
South Atlantic	24,200	2.9
Caribbean Sea	10,000	1.2
Gulf of Mexico	300	0.04
North Atlantic	243,400	29.2
North Sea	55,600	6.7
Pacific Ocean	255,000	30.6
South China Sea - Indonesia	53,500	6.4
TOTAL	771,500	92.54

[1] Blackman 1973; Finkelstein 1973, pers. comm.; Fairhall 1971. Estimates of distribution were obtained for the U.S.S.R. and U.S., Canada, Japan, France, and the U.K. were assumed to have the same distribution as the U.S. Other countries' navies were assumed to remain in their own coastal area.

[2] Assumes each ship is at sea 120 days/year.

Oil Platforms and Drilling Rigs

Oil platforms are primarily working rather than living areas. Disposal of waste from oil platforms and drilling rigs is strictly regulated in the U.S. and we assume that there is no release of litter (U.S. Department of Interior 1973b). We estimated the amount of activity as 50 person crews working 365 days a year for drilling rigs and 30 person-days per year for producing wells (Anonymous [Offshore 1973]), and litter generated per person-day as 0.5 (production platforms) and 0.67 (drilling rigs) of onshore values to yield 0.8 kg/person-day (production platforms) and 1.07 kg/person-day (drilling rigs). These values were based on estimates of the portion of a day a person was normally on a rig or platform obtained from oil and drilling companies. For total world off-shore oil production associated litter, we estimated 4.5 x 10^3 tons/year (Table 8-11).

Catastrophes

Catastrophic inputs were considered to see whether storms and accidents would exceed the estimates of litter from continuous sources.

In 1970 there were 2,353 ship casualties (Catholic University of America 1971), or a total tonnage of commercial ship loss of approximately 5 x 10^6 tons/year (Organization for Economic Cooperation and Development, hereinafter referred to as OECD, 1972). If the weight of cargo is equivalent to that of the net weight of the vessel (OECD 1972), 2.5 x 10^6 tons/year of cargo would be lost. However, a survey of the commodity list for several trade routes indicates that 96 percent of the cargo carried is ore, chemicals, vegetable products, or petroleum products (IMCO, Norway 1972), which were excluded from this analysis. Thus, we estimate that 10^5 tons per year of cargo classified as litter would be lost through casualty.

Relatively large amounts of local litter could be generated by natural catastrophes such as the storm in the Gulf of Mexico where 614 homes were lost (Marr 1973, pers. comm.), 90 were destroyed, and 483 sustained major damage (Bighinatti 1973, pers. comm.) (Table 8-12).

TOTAL ESTIMATES

We estimated the total amount of litter generated in the world's oceans per year on a continuous basis, assuming

TABLE 8-11

Man-Days at Sea Associated with Offshore Oil Production

Area	Mobile Drilling Rigs[1]	Producing Wells[2]	Estimated Total Litter Produced/Yr (10^6 kg)
Gulf of Mexico	71	8,556	1.6
Caribbean	13	7,844	0.4
Mediterranean	12	1,466	0.3
Persian Gulf	25	500	0.5
Indian Ocean	5	394	0.1
South Atlantic-Africa	16	329	0.3
South China Sea-Japan Sea	24	300	0.5
South Pacific	6	247	0.1
South America-South America	12	99	0.2
North Sea	26	10	0.5
TOTAL	210	19,745	4.5

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[1] McCaslin 1973.

[2] Anonymous (Offshore 1973).

[3] Litter generation rates:
(Rigs)(50 person crews)(365 days/yr)(1.07 kg/person/day)
+ (producing wells)(30 person-days/yr)(0.8 kg/person/day)

Litter produced should not be interpreted as released. In the U.S. disposal of waste from oil platforms and drilling rigs is strictly regulated (U.S. Department of the Interior 1973b). The degree of regulation in other areas is unknown.

TABLE 8-12

Damage to Dwellings in Disaster Areas of the Coastal United States in 1972

Area	Number of Homes Lost[1]	Number of Dwellings[2]			Number of Mobile Homes[2]	
		Destroyed	Major Damage	Minor Damage	Destroyed	Major Damage
Atlantic:						
Florida	-	23	334	1,728	-	-
Massachusetts	-	0	13	204	11	14
New York	1	0	-	-	-	-
Pennsylvania	0	-	-	-	-	-
North Carolina	0	-	-	-	-	-
Virginia	-	0	5	250	0	0
Maine	80	7	52	585	-	12
TOTAL	81	30	404	2,767	11	26
Hawaii:	0	-	-	-	-	-
West Coast:						
California	3	2	8	47	0	0
		3	12	621	0	26
Oregon	-	1	162	270	1	2
Washington	-	0	0	1	0	0
		2	8	11	0	2
TOTAL	3	8	190	950	1	30
Gulf of Mexico:						
Texas	91	0	20	110	0	0
	7					
	50					
Georgia	61	-	-	-	-	-
	218					
Alabama	102	-	-	-	-	-
	14					
Florida	6	90	419	1,191	12	211
Louisiana	13	0	42	94	0	0
Mississippi	52	0	2	143	2	13
TOTAL	614	90	483	1,538	14	224
U.S. TOTAL	698	128	1,077	5,255	26	280

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[1] Marr 1973, pers. comm.

[2] Bighinatti 1973, pers. comm.

that all trash generated was disposed of overboard, to be 6.4 x 10^6 tons (Table 8-13). However, this litter is not evenly distributed but is concentrated unevenly in the Northern Hemisphere. Eighty percent of marine merchant activity is within 400 km of land (U.S. Department of Defense 1964), fishing activities are concentrated over the continental shelves (Herring and Clarke 1971), and recreational boating activities are generally nearshore. Therefore, marine litter could be expected to be concentrated along coastlines.

TABLE 8-13

Total Litter Estimates

Source	Amount of Litter Generated (10^6 tons/year)
Passenger Vessels	0.028
Merchant Shipping	
Crew	0.110
Cargo[1]	5.600
Recreational Boating	0.103
Commercial Fishing	
Crew	0.340
Gear	0.001
Military	0.074
Oil Drilling and Platforms[2]	0.004
Catastrophe	0.100
TOTAL	6.360

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[1] We assume an unknown percentage of the waste is released in harbors, ports or nearshore areas.

[2] See footnote Table 8-11.

Better estimates of litter generation rates and input activities are needed. The Naval Shipboard Refuse Study (U.S. Department of Defense 1971) is a good example of trash-generation studies that should be made for other types of vessels.

OBSERVATIONS

We made a survey of world marine litter to assess the information available on the amounts of litter present. Table 8-14 presents a few representative samples from the survey. There are no consistent sources of quantitative litter data on a world-wide or national basis. Plastic objects are prominent in reports of litter sightings although they are a minor component of the total refuse generated.

We received responses to our inquiries regarding litter from a variety of sources and published reports which seem to indicate that litter distribution is uneven with concentrations forming at certain points.

FATES

Predicting the fate of marine litter involves knowledge of the rates of degradation of wood, paper, plastics, metals, and glass; and identification of the degradation products and pathways. Materials in the sea are subject to physical, chemical, and biological decomposition. A number of studies have described the effects of the marine system on a variety of substances, however, the results are highly dependent upon time and place. We were unable to predict the fates of litter because of the variability of the natural and human stressed marine environment and the general lack of data. For instance, petroleum contamination of an area may enhance the degradation of plastics but inhibit that of paper and wood.

EFFECTS

The physical effects of litter on equipment, which include the fouling of trawling nets by bottom debris such as wrecks, construction debris, and unburied well stems, can cause substantial economic loss to the fishing industry

TABLE 8-14

Selected Examples of Marine Litter Concentrations

Region	Area	Source	Information Contained
North Pacific	Amchitka	U.S. Department of Commerce 1973c	24,000 plastic items including 12 tons of polypropylene gill nets and 7,000 gill net floats per 60 miles of beach.
	North Central Pacific	Venrick *et al*. 1973	28 plastic fragments; 16 bottles; 9 miscellaneous man-made objects per 12.5 square kilometers.
	North Pacific transect	Wong *et al*. 1973, unpublished ms.	Plastics in 27/37 tows, 1 to 5 mm flakes of 20 to 30 mg; concentrations of 0.2 to 0.3/m^2. Paper, elastic bands, and wood off Japan Peak trough arrangement; high concentrations 140°W to 150°W, 35°N lat.
North Atlantic	U.S. East Coast - Cape Cod to Florida	Sherman *et al*. 1973	50% of the neuston samples had plastics in them; 1 mm diameter plastic beads; 3-5 mm diameter sheet disks; 2-4 mm pieces of styrofoam. Up to 13 grams per sample; cellophane sheets most widespread.

(Continued)

TABLE 8-14 (Continued)

North Atlantic (continued)	Long Island Sound to Vineyard Sound	Carpenter *et al.* 1972	0.1 to 2 mm clear crystalline polystyrene and opaque diene rubber polystyrene spherules found; highest average concentrations went up to $14/m^3$. Fish larvae containing plastics: Grubby 4.2% Winter Flounder 2.1% White perch 33% Silver sides 33%
Atlantic	Sargasso	Carpenter and Smith 1972	Average of 3,500 pieces or 290 $grams/km^2$; 2.5 to 5 mm diameter; one area with 12.080 pieces and 1,771 $grams/km^2$.
	Antilles	Sherman *et al.* 1973	38% of neuston samples had plastics.
	Caribbean	Sherman *et al.* 1973	20% of samples had plastics of light concentration.
North Sea	Northern Scotland	Scott 1972	690 and 1,130 pieces plastic/km beach; 71% polyethylene housewares; 7% L.D. polyethylene sheets; 7% polypropylene nets and ropes

(Continued)

TABLE 8-14 (Continued)

North Sea (continued)	Netherlands Continental Shelf	van Banning 1972	27-136 articles/km^2 benthic areas; 15-58% of these are man-made synthetic articles including; packing material, bottles, considerable broken glass and metal drums.
Gulf of Mexico	Padre Island National Seashore	McLaughlin 1973, pers. comm.	93 km stretch of beach; 129 55-gallon drums of industrial wastes; 3,500 blood donor kits; hardhats; plastics; shrimp boats and equipment; net floats; metal.

(Texas A & M University 1973). Lost fishing nets and trawling webs can damage ships by fouling screws and clogging water-intake pipes. Off Alaska, a large quantity of net is lost by foreign fishing vessels (Evans 1971, U.S. Department of Commerce 1973b, c, Sneed 1973, pers. comm., Stevens 1973). Large floating debris can be a navigational hazard.

In addition to these immediate threats of litter to our uses of the marine system, other potentially harmful effects have been observed but their long term impact has yet to be determined (Table 8-15).

Fishermen have long known that floating or suspended debris attract fish. Hunter (1968), working in the offshore waters of Costa Rica, suggested that floating objects attract fish because they function as schooling companions or as a substitute reef for those species which are not adapted to pelagic life. He observed that smaller fish appeared first at a floating object and larger species later. Kojima (1960) suggests that smaller fish are found with drifting materials because they are too small to resist currents, whereas the larger fish can resist currents and remain with fixed rafts.

The aggregation of fish about a floating or suspended object is rapid. Wickham (1972) observed 5 to 25 tons of baitfish attracted to an object within a day. He also found that floating objects 3 to 7 meters below the surface were more successful in attracting fish than those at the surface and that multiple structures were better than single ones.

Floating debris can also transport organisms into different ocean areas. Venrick *et al.* (1973) suggested the long-distance transport of sessile animals, algae, and bacteria to new areas by this mechanism. Floating materials such as styrofoam cups, six-pack retainers, and plastic bags may physically trap organisms, killing them or hindering their movements and feeding. Floating fragments of fishing nets and trawling webs can trap and drown marine organisms. For example, a large net found attached to the sunken *Andrea Doria* contained hundreds of fish in various stages of decomposition (Evans 1971). Of the 33,173 fur seals caught at St. Paul Island, Alaska in 1972, 81 had fragments of nets and 6 had ropes attached to them, 52 had plastic bands around their necks, and 76 had net marks on their flesh (Sneed 1973, pers. comm.).

TABLE 8-15

Potential Effects of Marine Litter

Types of Litter	Effects	Source
Floating debris	Attraction of pelagic fish	Hunter 1968, Hunter and Mitchell 1968, U.S. Department of Commerce 1973a, Kojima 1960, Wickham 1972
	Rafting of organisms	Venrick *et al.* 1973
	Fouling of screws and water-intake pipes and other ship damage	U.S. Department of Commerce 1973c
		Sneed 1973 pers. comm., Evans 1971, Stevens 1973
	Trapping of fish and birds	Evans 1971
Fishing nets	Killing of fish, drowning of diving birds, seals, and other mammals	Sneed 1973, pers. comm., U.S. Department of Commerce 1973c
	Entanglement and flesh damage of above organisms	Sneed 1973, pers. comm.
Bottom debris	Fouling of trawling nets	Texas A & M University 1973
	Hazard to submersibles	
	Attraction of bottom fish	Stone *et al.* 1973, unpublished data, Cooke & Hoyt 1971, Prince & Hoyt 1971, Salazar 1973, Brasher 1973

(Continued)

TABLE 8-15 (Continued)

Bottom debris	Shelter for smaller animals	Kottcamp and Moyle 1972
Small particles, fibers, elastics	Obstruction of the gut in puffins	Parslow and Jefferies 1972, Parslow *et al.* 1972
	Damage to fish gills, fins, and flesh	Woodward-Envicon, Inc. 1973, pers. comm., Sherman *et al.* 1973
	Possible intestinal blockage of small and larval fish	U.S. Department of Commerce 1973c, Carpenter *et al.* 1972, Evans 1971
	Clogging of gills of fish and crustaceans	Young 1973, U.S. Department of Commerce 1972a
	Accumulation in bird guts and possible blocking of alimentary tract	Rothstein 1973, Stevens 1973, U.S. Department of Commerce 1973c, Hayes and Cormons 1973, unpublished ms.

Elastic bands can be caught around the necks of small fish and damage the gills, flesh, and fins of the fish as it grows. Elastic threads have been found in the guts of puffins from Scotland and Norway (Parslow and Jefferies 1972). The elastic found in all these studies had retained its elasticity, indicating that little degradation had occurred. Rubber bands have been found on sturgeons in the Danube (Anonymous [*Mar. Poll. Bull.* 1971]) and on 29 percent of the sturgeons collected in the lower Mississippi (Woodward-Envicon 1973, pers. comm.).

Smaller particles (mm to cm size) may be ingested by small organisms. Suspended material can also clog the gills of fish and crustaceans beyond their capacity to clean them (U.S. Department of Commerce 1972b). Lobster and crabs grown in waters containing sewage sludge had their gills fouled with granular material (Young 1973). Small and larval fish have been reported to have polystyrene particles in their intestines (Evans 1971, Carpenter *et al.* 1972, Sherman *et al.* 1973), and larger fish may selectively feed on the white, opaque spherules (Carpenter *et al.* 1972). Similar plastic particles have been found in the gastrointestinal tracts of several birds (Rothstein 1973, Stevens 1973, U.S. Department of Commerce 1973c, White 1973, pers. comm.). Particles have also been reported in the regurgitated pellets from gulls and terns (Hays and Cormons 1973, unpub. ms.). Large bottom debris have been reported to attract fish (Cooke and Hoyt 1970, Brasher 1973). Kottcamp and Moyle (1972) describe freshwater sculpins using disposable cans for shelter and breeding.

The concentration of large quantities of debris in restricted areas can alter the normal movement of particles. For example, plastic bags and sheets tend to collect and stabilize sand on beaches.

OVERVIEW

From the data presently available, it is not possible for us to assess the damage from litter to the marine environment. Our estimates of litter generation and the data on effects suggest that existing concentrations of marine litter do not cause widespread significant alterations in the marine system. However, there may be deleterious effects in regions of litter accumulation. The primary overall impact of marine litter at this time appears to be aesthetic.

There have been few studies of the effects of litter on the behaviors of marine organisms and consequently we are unable to assess the potential impacts in this subject area.

We estimate that the flux of litter to the world oceans is 6.4×10^6 tons per year. This estimate is based on a series of assumptions and extrapolations of data collected for other purposes.

The proposed International Convention for the Prevention of Pollution from Ships limits the dumping of sewage and garbage from ships, prohibits the disposal of plastics, and sets mileage limits to prevent the discharge of other types of refuse close to land. If implemented, these restrictions will alter significantly our estimates of merchant shipping-associated litter.

The United States could be the source of approximately one-third of total world marine litter based on approximations of gross national product (World = U.S. times 3). Therefore, a major reduction in the U.S. input would not only directly affect the state of our own coastlines, but also that of the world ocean.

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